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UNIVERSITY OF ALBERTA

CHEMICAL ANALYSIS OF EDMONTON DRINKING WATER. DETERMINATION OF CHLORINE DIOXIDE IN DRINKING WATER

by

JOHN DYLAN PEAK

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

DEPARTMENT OF CHEMISTRY

Edmonton, Alberta

Fall, 1991

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THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

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This work is dedicated to the memory of my Grandmother

Abstract

This thesis is comprised of two sections. The first describes a sampling study of the drinking water distribution system of the City of Edmonton. The project was designed to set up and evaluate a sampling plan that would provide information on the location and frequency of sample collection to ensure adequate monitoring of the quality of the water. The plan included consideration of variability of the raw water source over the course of a year (from May 1988 to April 1989), especially during spring runoff periods when the organic content of the input water increases significantly, variability as a function of the plant producing the water, of the material comprising the pipes in the distribution system, of the storage reservoirs holding the water prior to distribution, and of the presence of dead ends in the distribution system. Samples were collected from reservoirs and from 21 fire halls throughout the city monthly for a year and analyzed for 15 parameters. A statistical analysis of the data showed that the system was in a good state of statistical control throughout the year, and that variations in water quality as a function of the factors listed above were too small to be significant. However, the results were useful in defining the chemical parameters that were most likely to vary with time of year and with location, and in providing a sound statistical basis for a working sampling program for the city laboratories.

In the second portion of the thesis, methods currently in use for the determination of trace levels of chlorine dioxide in drinking water during and after processing were evaluated, and a pair of spectrophotometric procedures using new indicator reagents were developed that provide increased sensitivity and convenience over present procedures. Screening of 13 compounds produced two, amaranth and evans blue, that possess high absorbtivity and are oxidized by chlorine dioxide but not by most other substances normally present in drinking water during and after processing. Since the oxidized form of each absorb little at the wavelength of maximum absorbance of the

original material, these dyes can be used as sensitive analytical reagents that provide reproducible results at chlorine dioxide concentrations as low as 5 parts per billion (micrograms per litre). In addition preliminary experiments indicate that these reagents can be used in a simple flow injection system that permits efficient and rapid measurements of chlorine dioxide suitable for routine applications.

Acknowledgements

I would like to thank my supervisor Byron Kratochvil for his kind assistance and enthusiasm throughout the project. I would also like to thank Kay Simpson for allowing me to use the facilities at the Rossdale Water Treatment Plant and also for her help in solving many of the problems that cropped-up during this work.

I would also like to thank the lab personnel at Rossdale for all their invaluable help and advice over the last three years, in particular Milton, John, Pearl, Margaret and Stan . Their patience in allowing me time on the instruments during periods of frenetic activity is much appreciated. I would also like to thank Inni Rashid and Pat Melnychuk of the process development team at the E.L. Smith plant for their advice and for the loan of some of their equipment in the latter stages of this project.

I would also like to thank my research group and my fellow graduate students in the department for making my stay here a pleasant one. In particular the members of the Chemistry soccer team (Slow Reactions) without whom sunday mornings will never be the same again.

Thanks also to my wife Sew for her patience and understanding throughout this work and for her invaluable help in typing parts of this thesis.

Finally I would like to thank the Chemistry Department of the University of Alberta, the City of Edmonton and Alberta Environment for their financial assistance during the course of this work.

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Chapter 1

Introduction

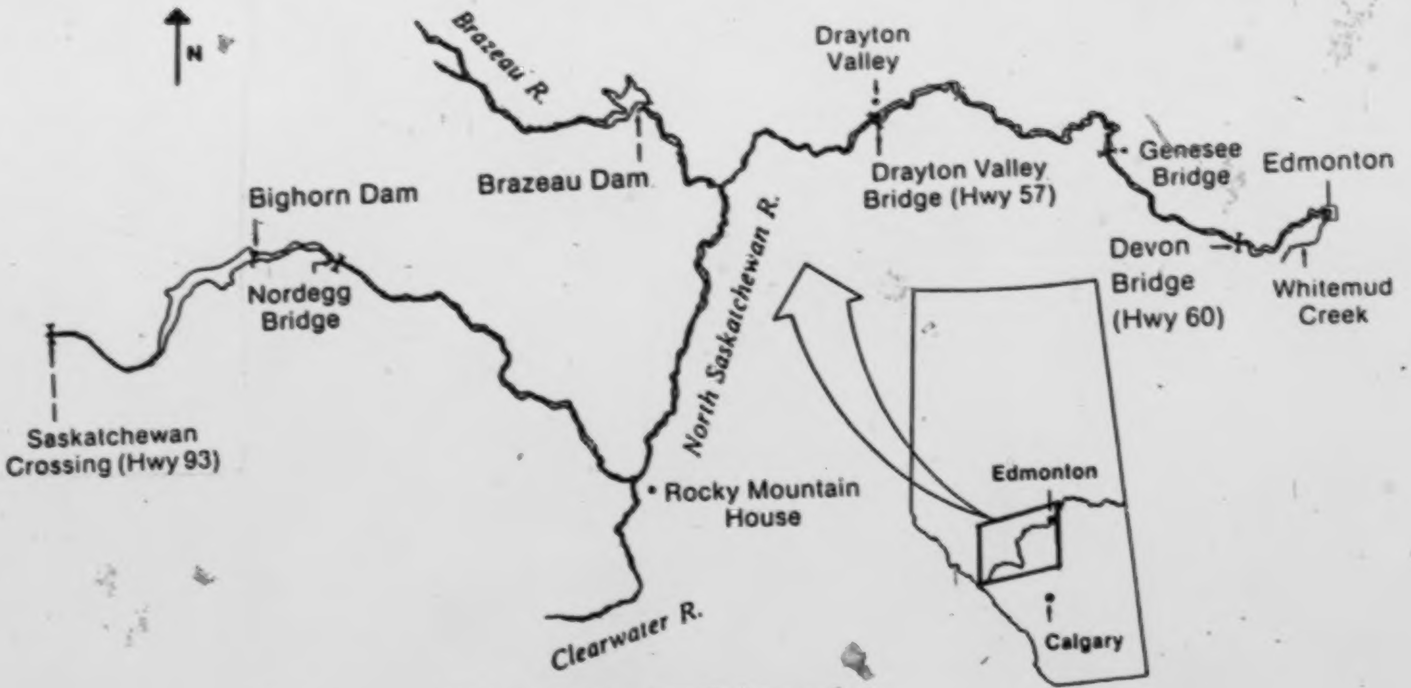
1.1.1 General

The City of Edmonton derives its water supply from the North Saskatchewan River (Figure 1.1). This river originates at the foot of the Saskatchewan Glacier, which is located 500 km west of the city in the Rocky Mountains. Water from glacier melt typically provides approximately 5% of the river`s flow in winter and up to 50% of the flow in July[1]. The major tributaries, the Clearwater, Brazeau, and Nordegg rivers contribute in varying amounts to the mainstream flow at different times of the year. Although water from glacier melt is normally of high quality, the water provided by these tributaries, which drain forested and muskeg areas, carry a higher organic load into the North Saskatchewan River. In addition several smaller streams, often with even higher organic content, join the River upstream of the City of Edmonton. As a result the overall quality of the raw water supply undergoes changes with seasonal conditions (for example during spring runoff). This places a heavy burden on the Edmonton water treatment facilities (Figure 1.2) at such times. Other contributing factors to poor water quality include water from the outfalls of the City of Edmonton storm sewer system which flows into the river predominantly during periods of rainfall.

In travelling from the Rockies to Edmonton, the river traverses through three distinct geological zones[2]. The first is the older Pre-Cambrian formations of the Rocky Mountains. The second is the Mesozoic rocks (sandstone, shale, and coal) of the foothills and the third is the formations of the Edmonton region. These are also of the Mesozoic era and also consist of sandstones and shales, but include as well minor bentonite formations.

Figure 1.1

The North Saskatchewan River Basin Upstream of the City of Edmonton.


N
Brazeau R.
Brazeau Dam
Bighorn Dam
Nordegg Bridge
Saskatchewan Crossing (Hwy 93)
Drayton Valley
Drayton Valley Bridge (Hwy 57)
Genesee Bridge
Edmonton
Devon Bridge (Hwy 60)
Whitemud Creek
North Saskatchewan R.
Rocky Mountain House
Clearwater R.
Edmonton
Calgary

Reproduced With Permission from Reference 6.

Figure 1.2

Location of the City of Edmonton Water Treatment Plants.

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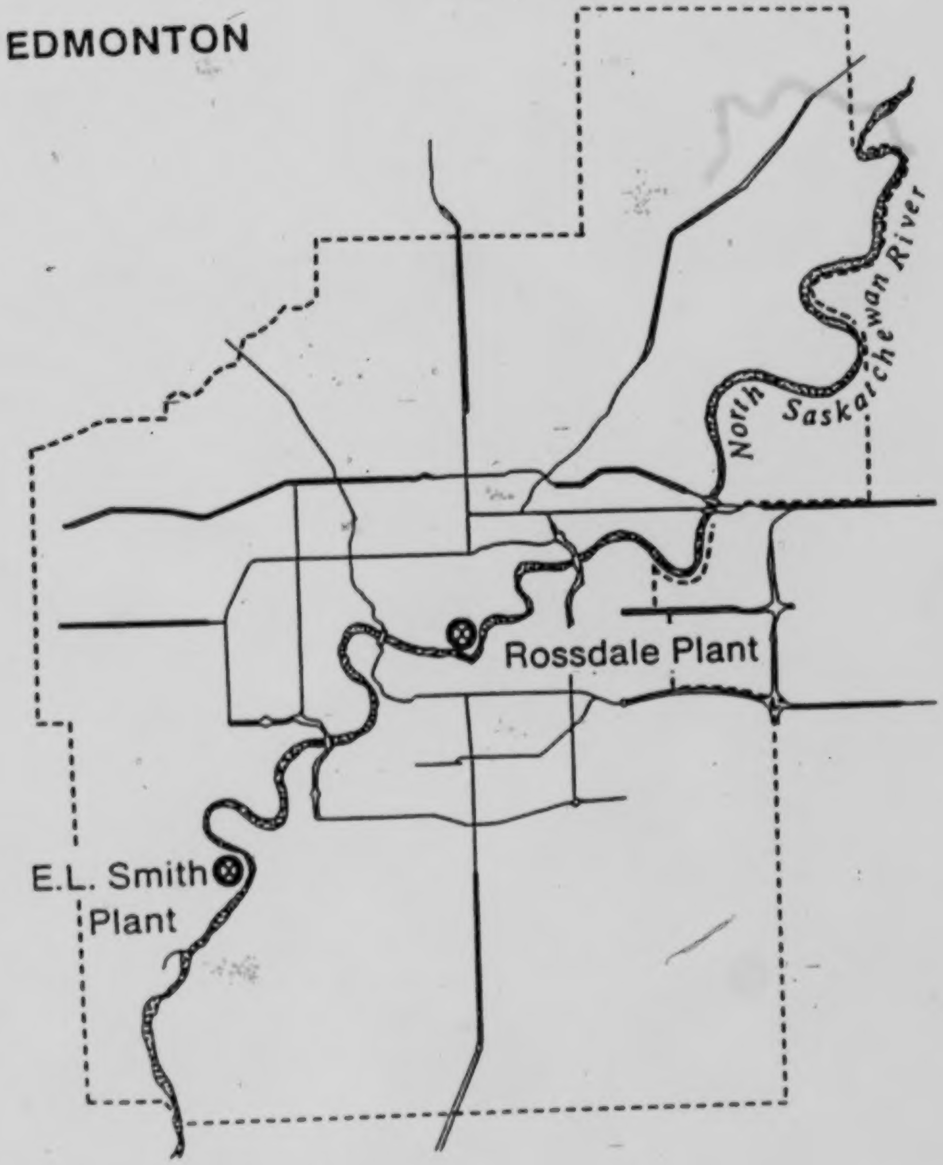

EDMONTON
North Saskatchewan River
Rossdale Plant
E.L. Smith Plant

1.1.2 The History of Water Treatment in Edmonton

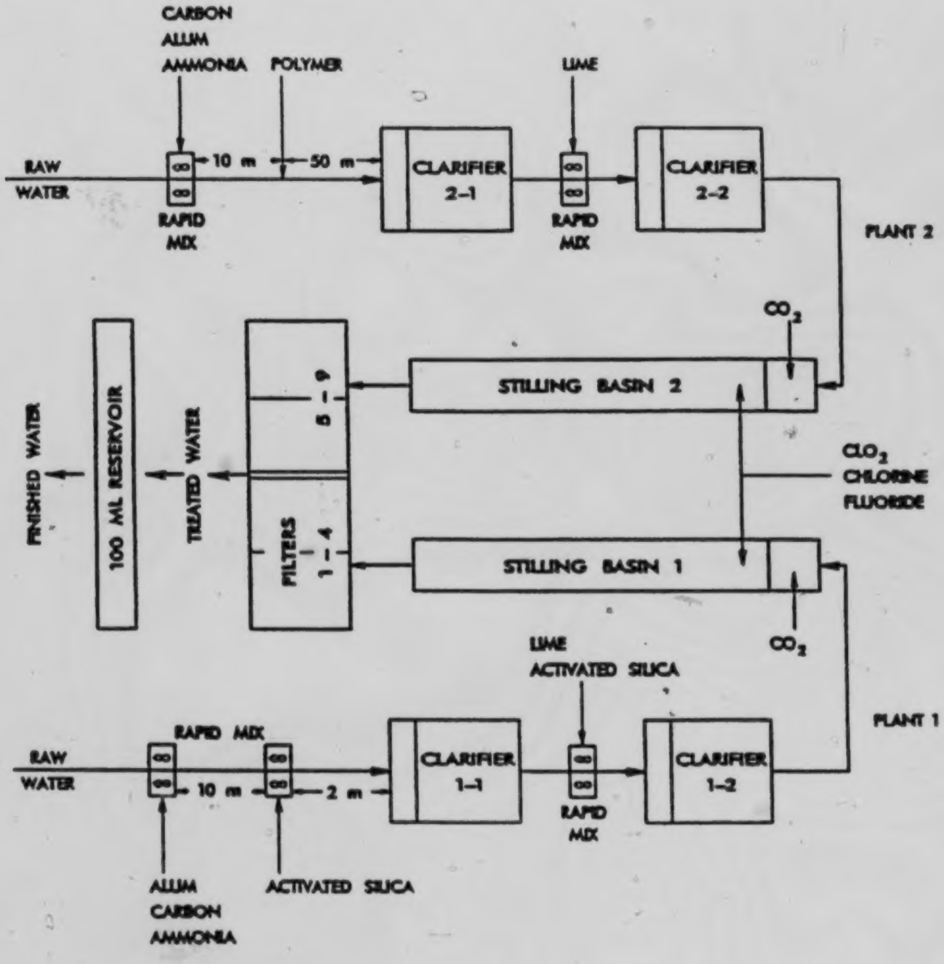
The first water treatment plant in Edmonton was built in 1903 and replaced a series of horse drawn wagons which had been used to deliver water (and coal) prior to that date. In 1947, oil was discovered in nearby Leduc and the city entered a period of tremendous growth. The Rossdale treatment plant was commissioned in 1947 (on the site of the old plant). This facility was expanded in 1956 to include a second plant (#2) and again in 1967 when a smaller satellite plant (#3) was commissioned. The three plants combined produce, on average 220 megalitres (ML) of treated water per day (based on 1986 data). In 1976 the modern E.L Smith plant (designated as plant #4) was brought into service to serve new suburban customers in expanding areas of the city. This facility underwent further expansion in 1983 and produces approximately 100 megalitres of treated water per day (based on 1986 data). A schematic of two of the Rossdale water treatment plants (plants #1 and #2) is shown in Figure 1.3.

1.2.1 The Water Treatment Process In Edmonton

The treatment process carried out at the Edmonton water treatment plants consists of the following operations: alum coagulation, clarification, chlorine dioxide and chloramine disinfection, fluoridation, and rapid sand filtration. Partial softening with lime and recarbonation is also practiced at plants #1, #2, and #4. Powdered activated carbon can also be fed at the point of alum addition as required for the removal of organic substances. These processes qualify as a complete treatment according to the Canadian Drinking Water Guidelines[3]. A more complete description of the water treatment process used by the City of Edmonton plants follows.

Figure 1.3

Process Schematic for Rossdale Water Treatment Plants #1 and #2.


CARBON
ALUM
AMMONIA
POLYMER
LIME
RAW WATER
10 m
50 m
RAPID MIX
CLARIFIER 2–1
RAPID MIX
CLARIFIER 2–2
PLANT 2
CO_2
STILLING BASIN 2
5 – 9
ClO_2
CHLORINE
FLUORIDE
FINISHED WATER
100 ML RESERVOIR
TREATED WATER
FILTERS 1 – 4
STILLING BASIN 1
CO_2
LIME
ACTIVATED SILICA
PLANT 1
RAPID MIX
RAW WATER
10 m
2 m
CLARIFIER 1–1
RAPID MIX
CLARIFIER 1–2
ALUM
CARBON
AMMONIA
ACTIVATED SILICA

(1) Water Intake

The intakes to the water treatment plants are located in the deepest part of the river next to the low lift pump stations. They are designed so that oils and surface debris will pass over the top and will not enter the plant.

(2) Screens

Just before the low lift pumps are screens which prevent larger debris from entering the intake. The screens have holes of about one square centimetre and are rotated and continuously cleaned by high pressure water.

(3) Low Lift Pumps

The low lift pumps are so called because they pump at a high volume but at a low pressure. These pumps operate at a rate of 20 to 40 megalitres (ML) a day and pump water continuously into the plant.

(4) Chemical Injection

In the first treatment step alum, ammonia, and occasionally powdered activated carbon are added. These chemicals are introduced as solutions or slurries via individual feed pumps designed to deliver the correct dosage to the water.

(5) Rapid Mix

This is achieved by a large propeller mounted on a shaft rotated by a 50 hp motor. The speed of the propellor required to achieve good mixing is of the order of several hundred revolutions per minute (rpm).

(6) Flocculation

The chemicals are next mixed slowly to allow the alum to form a floc[4,5] of net positive charge. This attracts negatively charged suspended colloidal particles and ultimately moves to the bottom of the settling basin. The flocculation section is designed to allow the floc to form and grow by controlling the flow rate of the water passing into the basin. Flow must be sufficiently slow and even so that the floc is not broken up before it has attained its optimum size. This step requires about half an hour for completion.

(7) Settling Basins

The dirt laden floc falls to the bottom and the clear water is decanted from the surface. The basins are designed so that the floc particles settle faster than the water "rises" in the clarifier (settling basin). This step in the process requires about an hour and a half to complete.

(8) Lime Addition

Lime (for softening) is now added at a level of about 55 mg/L (ppm), an amount sufficient to reduce the hardness of the water to around 115 ppm. After this addition the water again flows through rapid mixer, flocculation, and settling stages. However this time it is calcium carbonate (formed through the addition of lime) which settles out and is removed. The water spends approximately two hours in this section of the process.

(9) Recarbonation

The water now flows to the recarbonation chamber where carbon dioxide is bubbled through it to lower the pH. The carbon dioxide gas is generated under water by burning natural gas. The flow of the gas controls the rate at which the pH will be reduced.

(10) Chemical Addition

At this stage fluoride, chlorine, and chlorine dioxide are added by chemical injection. The fluoride, added as sodium fluorosilicate, is provided to reduce tooth decay. The latter two compounds are used in the disinfection process, the chlorine combining with the ammonia added earlier to form chloramines for long term disinfection in the distribution system, and the chlorine dioxide to act as an effective biocide and virucide to eliminate possibly harmful bacteria and viruses present in the raw water.

(11) Filtration

In the final step the water is filtered by allowing it to flow slowly through a layer of anthracite (about 30 cm thick) and then a layer of sand (about 50 cm thick). The filters are backwashed once a day by pumping water up through the filters and removing the material accumulated within them.

(12) Reservoir Storage

After filtration, the water is pumped to a storage reservoir until required, and then into the distribution system via a series of large high pressure pumps (high lift pumps). Each high capacity pump can pump up to 40 ML of water per day.

1.3.1 Project Aims and Initial Set-Up

The initial aim of the project was to design an optimum sampling program for the City of Edmonton water distribution system that would allow monitoring of the water quality in the system. This work was also intended as a follow-up study to a major review[6] of all aspects of the Edmonton drinking water system in 1986. In designing a sampling program parameters such as sampling site location and sampling frequency must be fully evaluated so that a sufficient number of samples are taken to ensure adequate monitoring. For sampling locations it was decided to use both satellite reservoirs (Figure 1.4), and fire halls (Figure 1.5) as primary sampling locations. These sites offered the advantage of easy accessibility and also provided good overall geographic coverage of the distribution system as a whole. An earlier plan to use fire hydrants as possible sampling locations was abandoned due to logistic problems such

Figure 1.4

Map of the City of Edmonton showing locations of reservoirs in the water distribution system. The location of the Burnewood booster station and the two water treatment plants are also indicated.

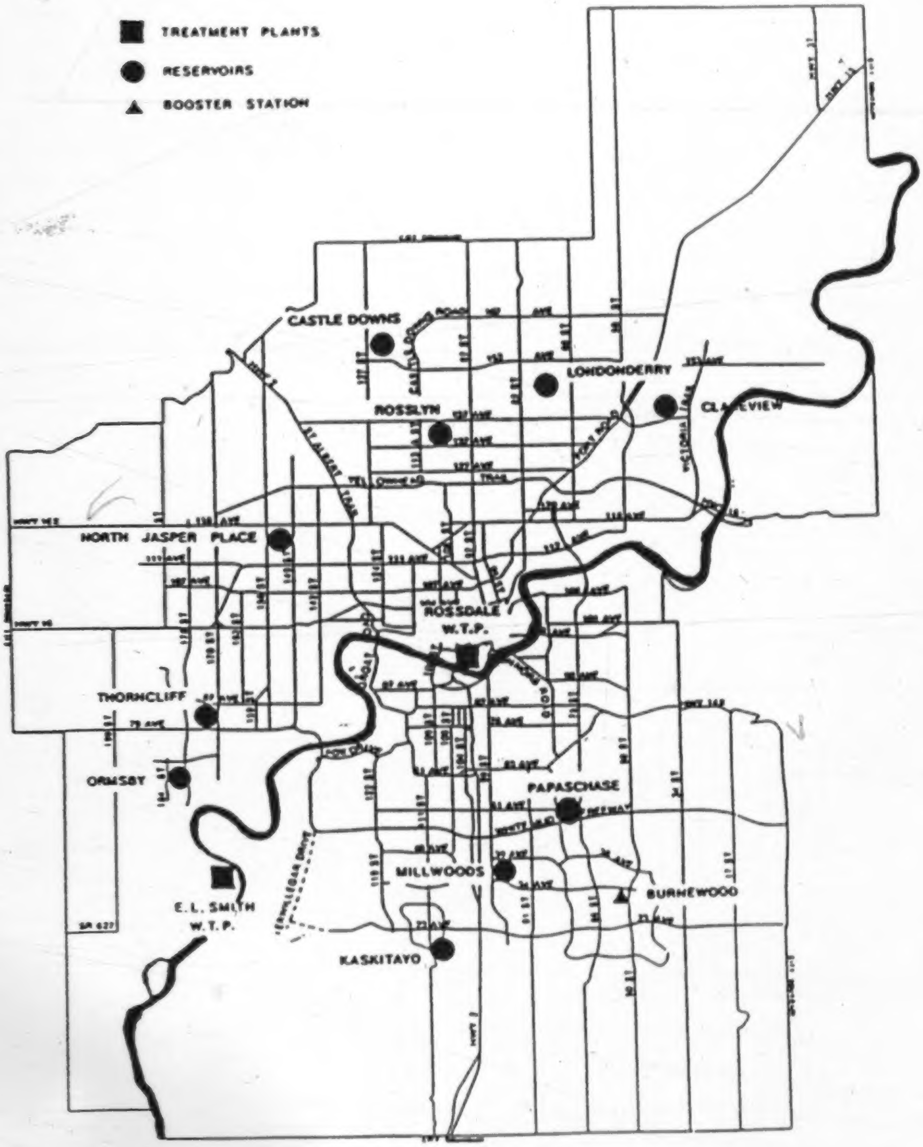
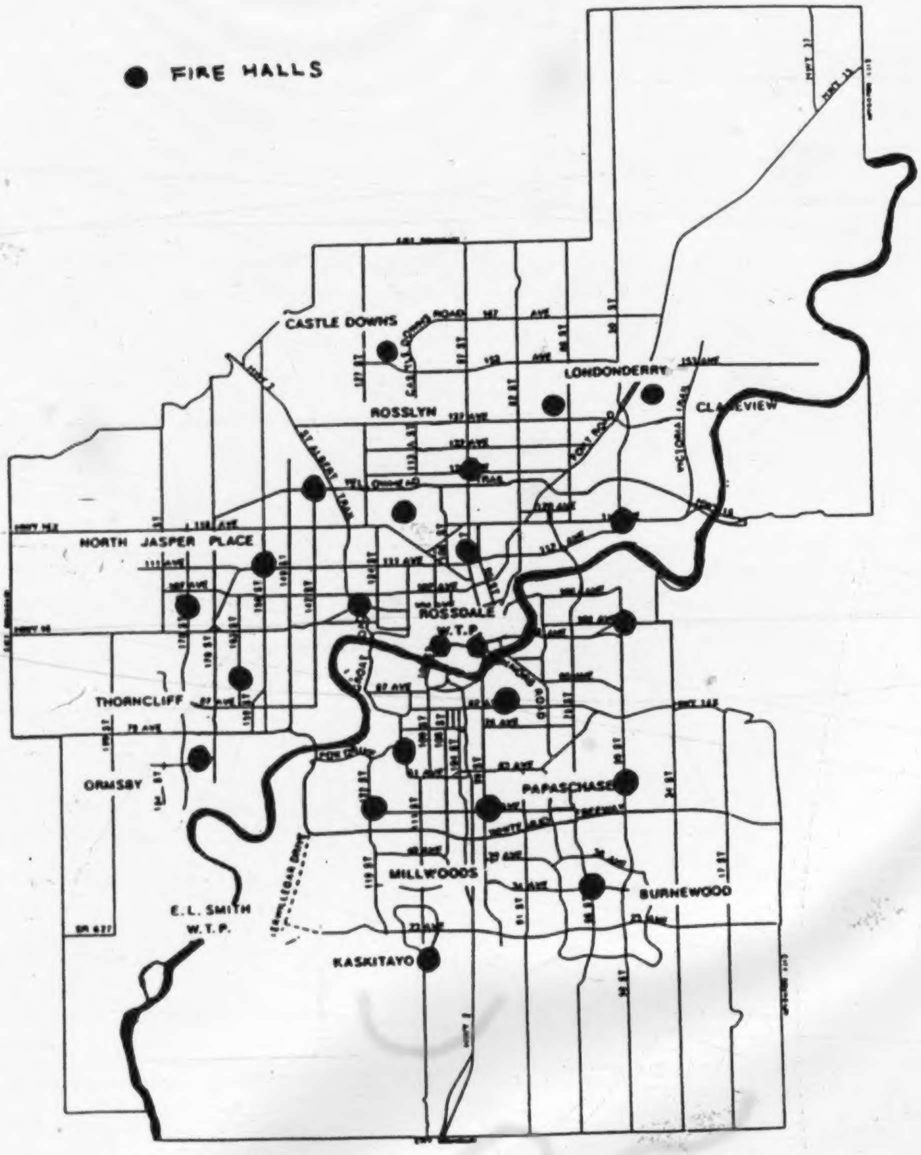

■ TREATMENT PLANTS
● RESERVOIRS
▲ BOOSTER STATION
CASTLE DOWNS
LONDONDERRY
CLAREVIEW
ROSSLYN
NORTH JASPER PLACE
ROSSDALE W.T.P.
THORNCLIFF
ORMSBY
PAPASCHASE
MILLWOODS
BURNEWOOD
KASKITAYO
E.L. SMITH W.T.P.

Figure 1.5

Map of the City of Edmonton showing locations of the fire halls used as sampling locations for the study of water quality in the distribution system.


FIRE HALLS
CASTLE DOWNS
LONDONDERRY
CLAREVIEW
ROSSLYN
NORTH JASPER PLACE
ROSSDALE
W.T.P.
THORNCLIFF
ORMSBY
PAPASCHASE
MILLWOODS
BURNEWOOD
E.L. SMITH
W.T.P.
KASKITAYO

as possible sample contamination and the problems associated with the operation of fire hydrants during periods of cold weather.

Several factors have been postulated to have potential adverse effects on water quality in distribution systems. These include the geographical location of the sampling site, which determines the time the water spends in the system, seasonal changes, and the nature of the pipe material through which the water flows. We were also interested in several so called "dead end" mains[7,8] which are found on the outer edges of the system and where several problems with poor water quality had been reported. The question of the effect of the pipe material on water quality is an interesting one; a number of studies have been carried out on this topic in recent years[9-12]. There are predominantly three types of pipe material in the Edmonton system: cast iron, asbestos cement, and polyvinyl chloride (PVC). The latter is now the material of choice and is currently being installed as part of a program to replace the cast iron mains which are beginning to corrode (much of the cast iron mains portion of the system was laid down early this century). As a secondary aim we also wanted to determine which of the chemical parameters measured on water samples on a routine basis in the city laboratory would be best for diagnosing possible problems in the system over the different seasons, especially during the annual spring runoff period in March and April. The progress made towards these objectives is detailed in the following sections.

Experimental Work

1.4.1 Introduction

A number of commonly measured chemical drinking water parameters were monitored in this study. These parameters can be classified into two categories, residuals (or non metals) and metals. The metals chosen for this study were those which are considered to be of broad environmental significance (such as lead[13] and cadmium) or those which are thought to be linked to potential human medical problems (such as aluminium which has been linked to Alzheimers disease[14]). A complete list of these parameters together with the relevant units is shown in Table 1.1. Water samples were collected in accordance with current ASTM guidelines[15], and were stored in standard one litre Nalgene (polyethylene) bottles. All samples taken from the system were analyzed within 24 hours (except for metal analyses) and prior to analysis were stored at 4°C in a refrigerator. Samples collected specifically for metal analysis were preserved by the addition of concentrated nitric acid (3 to 5 mL per litre of sample) and stored at room temperature until analyzed. Analyses of the residual parameters (see Table 1.1) was carried out with reference to available standards wherever possible and was in accordance with procedures outlined in Standard Methods[16]. All reagents and buffers employed in this work were used without pretreatment. Fluoride measurements were made using an Orion (model 9409) fluoride ion selective electrode (Orion Research, Cambridge, Mass) with a Fisher Accumet (model 950 MP) meter (Fisher Scientific, Nepean, Ont). Samples were maintained at a constant temperature to minimize hysteresis effects. All pH measurements were made using a glass electrode and a Fisher Accumet model 825 MP pH meter (both from Fisher Scientific, Nepean, Ont) calibrated with two buffers of known pH prior to use. Turbidity measurements were made on a Hach Turbidimeter (Hach Company, Loveland, CO) and readings were rounded up to the nearest 0.05 NTU (nephelometric turbidity units). Chloramine and oxidant measurements were made using a Wallace and Tiernan series A-790 amperometric titrator (Wallace and Tiernan). Organic carbon measurements were made on a Shimadzu 160 spectrophotometer (Shimadzu Corporation, Kyoto, Japan);

Table 1.1. Chemical Parameters Measured In This Study.

(a) Residuals (Non Metals)

Parameter	Units	Guideline Value[1]
Total Chloramines	ppm (as Chlorine)	> 1.8 ppm
Total Oxidants	ppm (as Chlorite ion)	< 0.5 ppm
Fluoride Ion	ppm	0.9-1.1 ppm
Turbidity	NTU[2]	< 1 NTU
pH		6.5-8.5
Total Hardness	ppm (as $CaCO_3$)	n/a[3]
Calcium Hardness	ppm (as $CaCO_3$)	n/a
Total Alkalinity	ppm (as $CaCO_3$)	n/a
Organic Carbon	HAU[26]	n/a

(b) Metals

Metal	Units	Guideline Value
Aluminium	ppb	n/a
Cadmium	ppb	5 ppb
Chromium	ppb	50 ppb
Copper	ppb	n/a
Iron	ppb	< 300 ppb
Lead	ppb	10 ppb

[1] Guidelines for Canadian Drinking Water Quality (see reference 3).

[2] Nephelometric Turbidity Units.

[3] No fixed guideline value has yet been assigned for this parameter.

samples were filtered through a standard 0.45 µm cellulose nitrate filter (Sartorius, Gottingen, West Germany) prior to analysis. All metal analyses were carried out on a Varian SpectrAA 300/400 atomic absorption spectrophotometer (Varian Techtron Ltd, Mulgrave, Australia) using a preset program and automatic sampler. A freshly prepared standard was used to produce (by dilution) solutions for a calibration curve for each set of samples run.

1.4.2 Methods of Analysis

The following is a description of the methods used and the principles behind the analysis of the various chemical parameters monitored in this study. It should be noted that all of the residual (non-metals) parameters are measured on a daily basis as a matter of routine on each new batch of finished drinking water produced in each treatment plant.

1.4.2.1 Total Chloramines and Total Oxidants

The analysis of total chloramines and total oxidants (essentially chlorite ion resulting from the decomposition of chlorine dioxide) is a measure of the disinfection residual in the distribution system. The method of analysis is a two step amperometric titration. In the first step the chloramines[17-19] (monochloramine, NH_2Cl, and dichloramine, $NHCl_2$) are determined as chlorine at pH 4. In the second step the total oxidants are determined as chlorite ion at pH 2. Both analyses are carried out on the same sample. The Wallace and Tiernan A-790 amperometric titrator used in this work has a special cell unit connected to a microammeter, with necessary electrical accessories. The cell unit includes a noble-metal (platinum) indicator electrode of sufficient surface area, a salt bridge to provide an electrical connection without diffusion of electrolyte, and a reference electrode of silver-silver chloride in a saturated sodium chloride solution connected into the circuit by means of the salt bridge. The indicator electrode is attached to a motor which rotates the electrode during titration. In this way the solution is constantly stirred. This type of electrode is often called a rotating platinum electrode (RPE).

The presence of an electroactive species in the cell produces a current and causes a deflection of the needle on the microammeter. The electroactive species in this titration is I_2 formed by reduction of the chloramines (represented as chlorine) by potassium iodide (KI), see equation 1. The iodine (present in solution in the form of the triiodide ion I_3^-) is titrated with standard phenylarsine oxide, which reacts with iodine in a molar ratio of 1 to 2 (equation 2). The amperometric end point occurs when all the iodine has been consumed and no current flows through the cell. At this point no deflection of the microammeter needle is observed upon the addition of further phenylarsine oxide.

$$Cl_2 + 2\,I^- = I_2 + 2\,Cl^- \quad (1)$$

$$I_2 + C_6H_5AsO + 2\,H_2O = C_6H_5AsO(OH)_2 + 2\,H^+ + 2\,I^- \quad (2)$$

Total Chloramines (as Chlorine)

Procedure. An aliquot of sample (200 mL) was measured into the titration vessel using a graduated cylinder. To this was added approximately 1 mL of 3M potassium iodide (KI) solution followed by 1 mL of pH 4 acetate buffer (Fisher Scientific, Nepean, Ont). This solution was placed in the cell and titrated to the amperometric end point with standard 0.00564 M phenylarsine oxide (PAO).

Total Oxidants (as Chlorite)

Procedure. To the same sample a sufficient amount of 6M hydrochloric acid (HCl) was added, with continuous stirring, to bring the pH of the solution to 2. The sample was placed in the dark for 5 minutes to allow the reaction (equation 3) to go to completion. The sample was returned to the cell and again titrated with standard PAO titrant to the endpoint.

$$ClO_2^- + 4\,I^- + 4\,H^+ = 2\,I_2 + Cl^- + 2\,H_2O \qquad (3)$$

Calculations.

(a) at pH 4

$$\text{mg/L (ppm) chloramines (as } Cl_2) = \frac{\text{mL PAO} \times M_{\text{titrant}} \times \text{EW (chlorine)}}{\text{V sample}}$$

where

mL PAO = Amount of PAO titrant required to reach the end point.

M (PAO) = Molarity of PAO titrant.

EW (chlorine) = Equivalent weight of chlorine (Cl_2) = 35453 mg/mol

V sample = Sample volume in mL.

(b) at pH 2

$$\text{mg/L (ppm) oxidants (as chlorite ion)} = \frac{\text{mL PAO} \times M_{\text{titrant}} \times \text{EW (chlorite ion)}}{\text{V sample}}$$

where

EW (Chlorite) = Equivalent weight of chlorite ion (ClO_2^-) = 16863 mg/mol

The equivalent weight of a species can be defined as the formula weight of a species divided by the number of electrons (n) transferred per molecule or ion during the reaction. In the first titration (at pH 4) the relevant reaction is:

$$Cl_2 + 2\,I^- \;=\; I_2 + 2\,Cl^- \qquad (1)$$

Here n = 2 and the equivalent weight of chlorine is thus 70906/2 = 35453 (mg/mole). The use of milligrams is to ensure that the units of the final answer are mg/L (ppm). Although the chloramines can be calculated in units of mg/L as chloramines, they are more usually reported in mg/L of chlorine to make the calculations more straightforward.

In the second titration (at pH 2) the oxidant is considered to be exclusively chlorite ion (ClO_2^-). The relevant equation is:

$$ClO_2^- + 4\,I^- + 4\,H^+ = 2\,I_2 + Cl^- + 2\,H_2O \qquad (3)$$

In this case n = 4 and hence the equivalent weight of chlorite ion is 67450/4 = 16863 mg.

The chemistry of these reactions and the use of amperometric titrations to determine halogen species will be discussed further in Chapter two of this thesis.

1.4.2.2 Fluoride Ion

The City of Edmonton adds sodium fluorosilicate to ensure a concentration of around 1 ppm of fluoride ion in the finished drinking water. Its function is to help prevent tooth decay in the general population. The fluoride ion concentration is measured potentiometrically through the use of a fluoride ion selective electrode (ISE) as the indicating electrode. In this electrode the sensor is a doped lanthanum fluoride crystal across which a potential is established by fluoride solutions of differing concentrations, one the sample solution and the other an internal reference solution. The overall cell can be represented as;

Ag/ AgCl, Cl^- (0.3M), F^- (0.001M) / LaF_3 / test solution / reference electrode.

The fluoride electrode can be used with a standard calomel electrode as external reference and any pH meter with an expanded millivolt scale. The electrode measures fluoride ion activity, which is related to the concentration of the ion through an activity coefficient term. The activity depends on the ionic strength, the pH, and the presence of possible fluoride ion complexing agents. The addition of a commercial solution available from Fisher (TISAB) to samples provides an essentially constant ionic strength, adjusts the pH, and ties up any fluoride ion complexing agents which may be present. Under such conditions the electrode reading may be considered a measure of the fluoride ion concentration rather than the activity.

Procedure. An aliquot (25 mL) of sample was transferred into a Teflon beaker containing a magnetic stirring bar and an aliquot (25 mL) of Total Ionic Strength Adjustment Buffer (TISAB), added to the sample solution to adjust the pH of the solution to an optimum value of around 5. The fluoride electrode was then calibrated by preparing two fluoride ion standards (in an identical fashion to the sample) having fluoride ion concentrations of 0.5 and 1.0 ppm. To make a measurement, the electrode system (fluoride and reference electrode) was immersed in the solution and the developed potential was measured while stirring at a constant rate with a magnetic stirrer. The solution was allowed to stir until a steady reading was obtained on the meter. Between solutions the electrode system was rinsed thoroughly with distilled water. To minimize hysteresis effects, the samples and standards were kept at approximately the same temperature (a range of 20°C ± 2 is recommended for reproducible analyses).

1.4.2.3 Turbidity

Turbidity in water is caused by suspended material such as clays or silts as well as by algae and other organisms. In treated water a high sample turbidity (>5 NTU) can indicate the presence of potentially harmful bacteria[20] and is thus an important parameter. Turbidity is measured by nephelometry in which a beam of light, usually from a tungsten filament lamp, is passed through a sample containing suspended particles. The radiation is scattered and the intensity of the scattered light at 90° to the incident beam is measured by a photomultiplier tube. The turbidity of the sample is thus directly proportional to the intensity of the scattered light.

Procedure. An aliquot of sample (25 mL) was transferred into a sample cell and placed into an ultrasonic bath to remove any air bubbles which may be present. Before measuring the sample the instrument was first calibrated by measuring the turbidity of a known commercial standard. The sample cell was placed into the instrument and the turbidity value recorded. A second reading of sample turbidity was then taken to ensure that consistent results were being obtained. The common units employed are Nephelometric Turbidity Units[16] (NTU). Results are normally rounded to the nearest 0.05 NTU.

1.4.2.4 pH Measurements

The pH of a water sample is one of the most commonly measured parameters. The current Canadian Drinking Water Quality Guideline[3] for the pH of finished drinking water is between 6.5 and 8.5. The pH is an important factor in calculating the so-called "Aggressiveness Index" of the water in the pipes. This topic will be discussed in more detail later in this chapter.

The majority of pH measurements are made using a system which consists of a potentiometer, a glass electrode, a reference electrode , and a temperature compensating device. A circuit is completed through the potentiometer when the electrodes are immersed in a test solution. The glass electrode has a bulb of special glass containing a fixed concentration of either HCl or a buffered chloride solution in contact with an internal reference electrode. When the electrode is immersed in an aqueous solution the outer bulb surface becomes hydrated and exchanges cations (sodium or lithium) for hydrogen ions until an equilibrium is reached. This, along with the repulsion of anions by negatively charged silicate sites, produces a potential at the glass-solution interface that is a function of the hydrogen ion activity in solution.

Procedure. The experimental procedure for the measurement of pH is straightforward. To calibrate the meter, buffer solutions of a known pH value were measured by placing a portion of the solution into a Teflon beaker and immersing the electrode system into the solution as it was being stirred by a magnetic stirrer. After a steady meter reading was obtained the meter was adjusted so the pH scale read the pH of the test buffer solution. Once this had been done the samples were measured, care being taken to rinse the electrodes with distilled water and blot them dry before immersing them into the next solution. Since pH measurements are temperature dependent, care was taken to ensure that the samples were at approximately the same temperature as the standards.

1.4.2.5 Total Hardness

At one time the hardness of water was loosely defined as a measure of the capacity of water to precipitate soap. Nowadays it is defined as the sum of the magnesium and calcium ion concentrations, expressed in mg/L (ppm) as calcium carbonate[21]. The water hardness value is determined by titration with EDTA.

Ethylenediaminetetraacetic acid (EDTA) forms soluble chelate complexes with most metal ions. If an indicator such as calmagite is added to an aqueous solution containing calcium and magnesium at a pH of 10 ± 0.1, the solution becomes wine red owing to the formation of a Mg-calmagite complex. If EDTA is added as a titrant the calcium and magnesium are complexed by the EDTA. When all of both species are complexed the first excess EDTA removes the magnesium from the indicator and the solution turns sky blue, indicating the end point. Since magnesium is required for a sharp end point a small amount of the complexometrically neutral magnesium salt of EDTA is usually added to the titrant solution. This ensures the presence of sufficient magnesium for optimum end point determination and at the same time eliminates the need for a blank correction.

Procedure. An aliquot of sample (50-mL) was measured using a graduated cylinder and transferred into a porcelain dish. A graduate is used because a precision of about one percent is adequate in this work. To the sample was added 1 to 2 mL of commercial pH 10 buffer (H-2, Alchem Ltd, Burlington, Ont) which contains ammonium chloride, ammonium hydroxide, and the magnesium salt of EDTA. A small amount of H-3 powder (Alchem Ltd, Burlington, Ont) was added to the sample. This powder contains calmagite indicator plus a small amount of sodium cyanide to mask possible interferences by other metal ions. The addition of this powder produces a purple/red solution which was titrated (with constant stirring) with standard 0.01M EDTA. As mentioned previously the end point is reached when the color of the solution becomes sky blue.

Calculation.

$$\text{Total hardness (as mg/L } CaCO_3) = A \times B \times 1000 / V_{sample}$$

where

A = mL of EDTA titrant required in the titration.

B = mg $CaCO_3$ equivalent to 1.00 mL of 0.01M EDTA titrant.

Vsample = Sample Volume (50 mL).

Since the formula weight of $CaCO_3$ is 100000 mg, 1 mg is equivalent to 1.00 mL of EDTA. Since the sample size is 50 mL and B=1, and thus the formula above reduces to;

Total hardness (as mg/L $CaCO_3$) = A x 20

Values of total hardness are reported to the nearest whole number.

1.4.2.6 Calcium Hardness

Calcium in water supplies generally results from water passing over or through deposits of limestone, dolomite, or similar minerals. The presence of calcium carbonate in the water, as well as magnesium carbonate, helps to prevent corrosion of pipes by laying down a protective coating on the inner surface of the pipe[22,23]. The extent to which this occurs depends on the alkalinity of the water flowing in the pipes. However, excessive quantities of calcium bicarbonate or sulfate salts can on heating form scale in boilers or cooking utensils. This process can often be reversed by water softening treatments involving ion exchange or similar processes.

Calcium hardness is also determined by an EDTA titration. To avoid interference by magnesium the pH of the sample is raised to 12 to 13 to precipitate magnesium as the hydroxide. Use of a indicator selective to calcium, generally Eriochrome Blue Black R, or Calcein, enables calcium hardness to be determined quickly and easily.

Procedure. A 50-mL aliquot of sample was measured using a graduated cylinder and transferred into a porcelain dish. The pH of the sample was raised to 12 by the addition of 2 mL of 1.0 M sodium hydroxide and sufficient (0.1 to 0.2g) Eriochrome Blue Black R indicator (obtained commercially in the form of a powder from Alchem Ltd, Burlington, Ont) was added to give the solution a pink coloration. The sample was titrated with 0.01M EDTA to a purple end point. The calculation is analogous to that for total hardness and has the same units of mg/L as $CaCO_3$.

1.4.2.7 Alkalinity

The alkalinity of water refers to its acid neutralizing ability, but it can also be defined as the sum of all titratable bases. Alkalinity measurements are used to calculate the "Aggressiveness Index" of water (see section on pipe materials) and as such are an important tool in process control. The most common bases present in drinking water are hydroxide (OH^-), carbonate (CO_3^{2-}), and bicarbonate (HCO_3^-); of these the latter two predominate. Alkalinity is determined by a direct acid-base titration in which a combination of bromocresol green and methyl red is used as indicator.

Procedure. A 50-mL aliquot of sample was measured using a graduated cylinder and transferred into a porcelain dish. Bromocresol green-methyl red indicator was added (The indicator solution is prepared by mixing two parts of a 0.04 % solution of the sodium salt of methyl red with 3 parts of a 0.04 % solution of the sodium salt of bromocresol green, both solutions being prepared in ethanol.). The resulting green solution was titrated with 0.02 M sulfuric acid to a permanent pink. The sulfuric acid was standardized against primary standard sodium carbonate.

Calculation

Alkalinity (as mg/L $CaCO_3$) = mL of acid required for titration x 1000 / V sample (mL).

1.4.2.8 UV Measurement (Soluble Organic Carbon)

Water from the North Saskatchewan River contains measurable quantities of soluble organic carbon from various sources. This organic carbon is often in the form of derivatives of humic and fulvic acids[24,25], which are complex organic molecules whose structures have not been completely evaluated. The water treatment process cannot remove all of this organic material and significant concentrations of this material may remain after processing. The net result of the presence of these and other organic compounds which are present in the water in trace levels is a decrease in water quality at various times in the year, especially during the spring runoff period. Some information on the level of soluble organic carbon may be obtained by a UV method developed "in house" by staff members at the Rossdale Water Treatment Plant of the City of Edmonton[26]. The UV absorbance at 200 nm is measured on a filtered sample. This absorbance is converted to a concentration of humic acid via a standard calibration curve prepared from a commercial humic acid standard. It should be noted that this method is not a standard method and has its limitations, for example it will not respond to the presence of organic compounds which do not absorb at 200 nm. However it does provide some information of the levels of humic material which are present in the water and is a good indicator of the onset of rural runoff periods (see section 1.5.5).

Procedure. A 100-mL aliquot of sample was taken and filtered under vacuum through a standard 0.45 μm pore size cellulose nitrate membrane filter. The spectrophotometer (Shimadzu model 160) was zeroed at 200 nm by placing 4-cm quartz sample and reference cuvettes, both filled with filtered distilled water in the sample holders and setting the absorbances to zero with the autozero function of the instrument. The sample cuvette was removed and filled with the filtered water sample. The absorbance was then recorded and converted to concentration by reference to a standard calibration curve. The calibration curve was prepared from a characterized fulvic acid material obtained from Cooper Langford of the Department of Chemistry, Concordia University, Montreal, Quebec. Since the presence of air bubbles in the sample can have an effect on the measured absorbance the filtered sample was allowed to stand for 10 to 15 minutes before measurement.

The measurement of soluble organic carbon concludes the procedures for residual (non metal) parameters. The remaining parameters measured in this study, those of the metals, were done by graphite furnace atomic absorption spectrometry (GFAAS), and are discussed in the next section.

1.4.2.9 Analysis of Metals by Atomic Absorption

Atomic absorption is one of a group of analytical techniques known generically as atomic spectroscopy. In atomic spectroscopy, samples are vaporized at high temperatures and the concentrations of selected atomic species are determined by measuring either their absorption or emission of radiation at selected characteristic wavelengths. The high sensitivity and excellent selectivity of these methods are due to the very narrow spectral bandwidths of the emissions of gaseous atomic species. As a result atomic spectroscopy has become one of the principal tools of analytical chemistry. Analyte concentrations at the parts-per-million (ppm) and parts-per-billion (ppb) level can be measured on a routine basis with a precision typically of the order of one percent.

In conventional atomic absorption spectrometry (AAS) a sample solution is aspirated into a flame at a temperature of 2000 to 3000 K, whereby the sample molecules undergo atomization. To measure the absorbance of radiation emitted by, say, excited iron atoms in the flame, the light source used is often a cathode containing that element. This source, known as a hollow cathode lamp, emits light with the characteristic frequencies of iron atoms as they return from excited states to lower energy states. This radiation is readily absorbed by ground state atoms of the sample in the flame, and gives rise to the phenomenon of atomic absorption. The measured absorption is directly proportional under optimum conditions to the concentration of the metal atoms in the sample.

The use of an electrically heated tube furnace instead of a flame for atomization of the sample offers greater sensitivity and requires a much smaller amount of sample. The tube furnace, usually made of graphite, is mounted between the hollow cathode lamp and the detector of the spectrometer in place of the flame. For a typical analysis using a graphite furnace, sample volumes of the order of 1 to 100 μL are injected into the furnace through a small hole in the center of the tube wall. In practice this is done by an autosampler to ensure reproducible injection volumes. To allow the light beam from the hollow cathode lamp to pass through the furnace, each end of the tube is open. The enhanced sensitivity of the graphite furnace technique arises because the entire sample is confined within the light path for several seconds. In flame spectroscopy the sample is highly diluted before it reaches the flame and, in addition, the atoms spend only a fraction of a second in the light path. Furnaces are, however, in general less precise than flames and require more work to determine the optimum conditions for each species. This is because the furnace must be heated in stages to ensure the solvent and easily combusted components of the sample are vaporized before the element of interest is atomized. The heating stages are drying (to remove solvent), charring (to remove organic material or other interfering matrix components), and atomization, in which the sample is heated strongly for a short time to vaporize all remaining material. It should be noted, however, that more than one temperature step may be required to complete each stage in the process. During atomization the absorbance reaches a maximum and then decreases as the sample evaporates from the furnace. Either maximum absorbance, peak area, or peak height may be measured as the analytical signal.

In this study six metals were determined on a Varian SpectrAA 300/400 atomic absorption spectrometer, equipped with a Varian GTA-96 graphite tube atomizer and autosampler. The experimental procedure used for the analysis for each of the various metals was essentially identical and therefore will be described in detail for only one, copper. Details of the program, including furnace and sampler parameters, used for copper are shown in Table 1.2. Details of the programs used for the analysis of the other metals can be found in Appendix II. The spectrAA system is microprocessor controlled and can store up to 40 programs in its memory. All relevant parameters for the analysis of a particular metal are stored on one program that can be recalled prior to analysis; this ensures all instrumental parameters are already preset.

Procedure. The initial step was to prepare a standard solution by dilution of a higher concentration stock solution. Several levels of dilution were often necessary to obtain the required concentration. Standards and samples should have approximately the same matrix to minimize interferences. For copper analysis a 0.025 mg/L (25 ppb) standard was prepared by successive dilutions of a 25 mg/L standard, which in turn was prepared by dilution of a 1000 mg/L atomic absorption copper standard (BDH, Toronto, Ontario). The dilute standard contained 3 to 5% concentrated nitric acid to approximate the matrix of the samples. Prior to preparing the standard the copper program containing the preset instrumental parameters was recalled from the memory of the microprocessor.

Once the standard had been prepared and sufficient time (20 to 30 mins) had been allowed for the hollow cathode lamp (HCL) to stabilize, a distilled water blank was placed in the autosampler tray and several autosampler injections made to zero the instrument. The autosampler can be programmed to make serial dilutions of the standard (see Table 1.2) to produce a calibration curve. Once the instrument had been zeroed the standard and samples were loaded onto the autosampler tray and the analysis started.

Table 1.2

SpectrAA 300/400 parameters used in the analysis of copper (Cu) by Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS).

(a) Instrument Parameters

Instrument Mode	Absorbance
Calibration Mode	Concentration
Measurement Mode	Peak Height
Lamp current (mA)	4
Slit Width (nm)	0.5
Wavelength (nm)	324.8
Time Constant	0.05
Measurement Time (s)	1.0
Replicates	3

(b) Furnace Parameters

Step Number	Temperature (°C)	Time (sec)	Gas Flow (L/min)
1	85	5.0	3.0
2	95	50.0	3.0
3	120	10.0	3.0
4	800	2.0	3.0
5	800	15.0	3.0
6	800	1.2	0.0
7	2000	1.0	0.0
8	2000	1.2	0.0
9	2000	2.0	3.0
10	2000	1.5	3.0

(c) Sampler Parameters

Solution	Conc (ppb)	Solution (μL)	Blank (μL)	Vtotal (μL)
Blank		0	25	25
Standard 1	1.0	1	24	25
Standard 2	5.0	5	20	25
Standard 3	10.0	10	15	25
Standard 4	15.0	15	10	25
Standard 5	25.0	25	0	25
Sample		25	0	25

The experimental procedure for the other metals was analogous to that outlined for copper except for aluminium, where it was necessary to dilute the samples by a factor of ten to bring them into the optimum range of the calibration curve. Occasional samples of other metals, such as iron, that fell outside the range of the standard calibration curve were diluted by a factor of ten and re-run. Dilute standards were freshly prepared as outlined above on a daily basis prior to analysis and were discarded once the analysis had been completed. Quality control was monitored by running standards and "spikes" along with the samples to ensure reproducible data was being obtained.

This concludes the section outlining the experimental methods used for the analysis of the chemical parameters. The next section will deal with the statistical analysis of the data collected during the course of this study (May 1988-April 1989).

Analysis of the Data

1.5.1 Overview

The data collected during this study, along with the sampling dates for the various sites, is shown in Appendix 1. No data was collected by the author from the fire halls during August 1988; the data recorded for the reservoirs during that month was collected by the City of Edmonton laboratory staff. Three fire halls (#14, #18, and #21) were not sampled during the course of this study because these locations are adjacent to city reservoirs (see Figures 1.4 and 1.5) and hence sampling these locations would have meant site duplication. Analysis of the metals in samples taken from the reservoirs was started in June 1988, and in samples from the fire halls in July. The levels of many of the chemical parameters monitored during the course of this study are to a large extent fixed during the water treatment process itself and are thus under close control at the time the water leaves the treatment plants. Any variability in these parameters should arise, therefore, primarily from reactions occuring while the water is in the distribution system. In the following section several aspects of the distribution system will be discussed. These include a statistical study of the City of Edmonton water analysis data to determine whether characteristics of the water produced at the two treatment plants are significantly different, a study on the possible effect of pipe materials on water quality, and a study of "dead end" locations. In addition, the effect of the annual spring runoff in April 1989 on several parameters was assessed.

1.5.2 Treatment Plant Study

As stated previously the City of Edmonton has two treatment plants, Rossdale and E.L. Smith. In general the Rossdale plant services the central and north-east regions of the city whereas the Smith plant services the suburban and southwest areas. Parts of the city (i.e Millwoods) can receive water from either or both treatment plants; for the purposes of this study these areas are referred to as "mixed" supply zones. Following several discussions with members of the city water engineering branch an approximate map of the supply zones of the treatment plants was constructed (Figure 1.6) that enabled the sampling sites to be assigned to the correct supply zone.

Once the sites had been assigned, monthly averages and standard deviations were calculated for all parameters. The reservoir and fire hall data for the two treatment plants were evaluated separately so that direct comparisons of the two plants could be made. When calculating averages, data from the "mixed" zone were not used. The assignment of sampling sites to supply zones is given in Table 1.3.

Data summarizing average monthly values for the Rossdale and Smith sites can be found in Appendix 1. The average (mean) values were obtained by summing all values obtained for a particular parameter in a given month and dividing by the number of sites from which the data was collected. For example, to calculate the mean value of

Figure 1.6

Approximate Supply Zones for the City of Edmonton Water Treatment Plants.

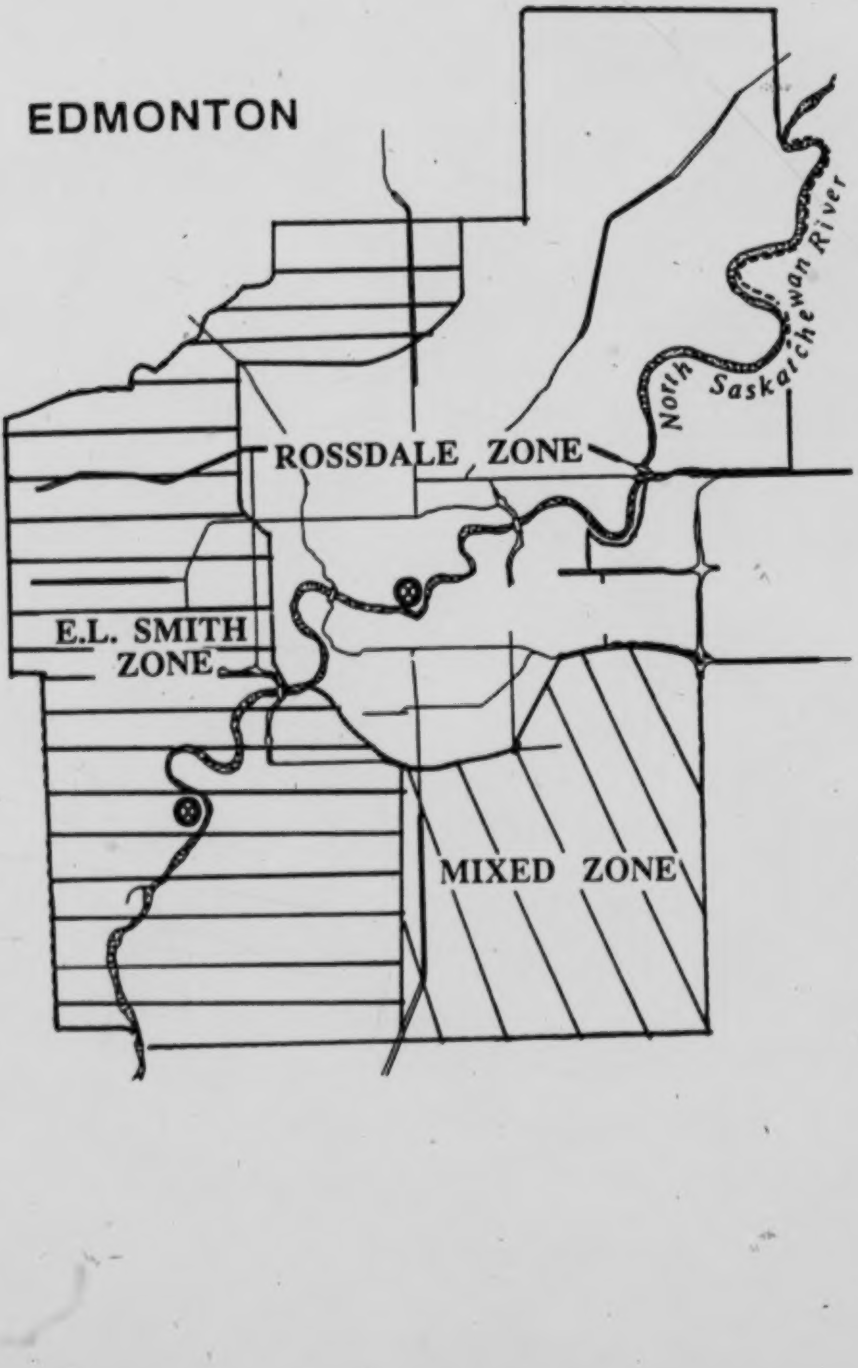

EDMONTON
ROSSDALE ZONE
E.L. SMITH ZONE
MIXED ZONE
North Saskatchewan River

Table 1.3

Assignments of the sampling sites used in this study to supply zones.

(a) Reservoirs

Rossdale Zone (5)	**E.L Smith Zone (4)**	**Mixed Zone (4)**
Clareview	Kaskitayo	Millwoods
North Jasper Place	Castledowns	Papaschase #1
Rosslyn #1	Ormsby Place	Papaschase #2
Rosslyn #2	Thorncliff	Burnewood Booster
Londonderry		

(b) Fire Halls

Rossdale Zone (13)	**E.L Smith Zone (6)**	**Mixed Zone (2)**
#1	#12	#9
#2	#13	#16
#3	#17	
#4	#19	
#5	#20	
#6	#23	
#7		
#8		
#10		
#11		
#15		
#22		
#24		

the total chloramines from the Rossdale zone fire halls in November the data collected from all the fire halls (one sample per month from each fire hall) was summed and divided by the number of sites (13 in this case). A number of graphs of the mean monthly value versus time for certain selected parameters were plotted; these also can be found in Appendix 1. Error bars on these plots represent the standard deviation of the mean value obtained for that parameter for the month shown on the x-axis. Note that for iron it was necessary to eliminate those values which fell outside the range of the calibration curve before calculating the average. This was done so as to not unduly bias the results by including sites where possible contamination problems were suspected (consistently high iron values found at Rosslyn #1 reservoir are thought to be the result of contamination from the sampling line) and also to ensure that graphs having comparable axes could be plotted.

The data were evaluated by analysis of variance. An analysis of variance[27,28] (ANOVA) study employs tests based on variance ratios to determine whether or not statistically significant differences exist between the means of several groups of observations (assuming each group follows a normal distribution). By using a one way analysis of variance procedure to determine the effect of a fixed or independent variable (treatment plant) on a dependent variable (a water parameter) we hoped to establish whether there was in fact any significant difference between the output of the two treatment plants for the different chemical parameters. Five parameters were selected for study by ANOVA, total chloramines, turbidity, organic carbon, copper, and iron, because each exhibited some degree of variation over the period of the study (Appendix 1). A number of separate ANOVA studies were carried out on the reservoir and fire hall data, which covered periods spanning several months (Table 1.4). The computer program Statworks (Datametrics Inc) was used to calculate the F-ratios for each ANOVA study.

The F-ratio, sometimes referred to as the variance ratio[27], compares the variance between data sets to the variance within data sets. The calculated F-ratio (F calcd) is compared with a tabulated value (F table) at the desired confidence level, taking into account the relevant number of degrees of freedom associated with the within and between ratio terms. The number of degrees of freedom is given by the quantity (n-1), where n is the number of measurements in the data set.

For an ANOVA study to conclude that a statistically significant difference exists between the variables under consideration, the calculated F-ratio (F calcd) must be numerically greater than the tabulated value (F tab). The results of the treatment plant study (Table 1.4) were negative (at the 95% confidence level) for all the comparisons but one. The only exception occurred for organic carbon for the fire halls during the period May to July 1988. The cause of this exception can be found by examining the cumulative monthly average data for the fire halls (Appendix 1), which shows that during the three months of the ANOVA study the monthly average for organic carbon for the Rossdale fire halls is higher than for the Smith fire halls, leading to a statistically significant difference in organic carbon values during this period. The reason for this difference is not clear. One explanation for this is the raw water quality at the Rossdale intake is generally poorer than at the Smith plant due to the presence of storm sewers and other urban runoff sites which are closer to the Rossdale water treatment plant.

Overall, from the results of these studies we can conclude that with the exception of the levels of organic carbon there are no significant differences between the outputs of the two water treatment plants for any of the parameters studied. This conclusion can probably be extended to cover all the parameters studied in this work because visual

Table 1.4

Summary of ANOVA[1] results for the treatment plant study.

(a) Reservoirs

Parameter	Study 1	F calcd	F table
Total Chloramines	May-August	0.84	4.12
Turbidity	May-August	1.63	4.12
Organic Carbon	May-August	3.90	4.12
Copper	June-October	0.40	4.16
Iron	June-October	0.33	4.17

Parameter	Study 2	F calcd	F table
Total Chloramines	December-February	0.88	4.14
Turbidity	December-February	0.33	4.14
Organic Carbon	December-February	2.33	4.14
Copper	November-March	2.65	4.08
Iron	November-March	0.41	4.10

(b) Fire Halls

Parameter	Study 1	F calcd	F table
Total Chloramines	May-July	0.086	4.04
Turbidity	May-July	0.74	4.04
Organic Carbon	May-July	6.60	4.04
Copper	July-October	0.034	4.01
Iron	July-October	0.004	4.01

Parameter	Study 2	F calcd	F table
Total Chloramines	December-February	3.31	4.02
Turbidity	December-February	0.081	4.02
Organic Carbon	December-February	3.15	4.02
Copper	November-March	3.66	3.96
Iron	November-March	0.21	3.96

[1] At the 95% level of confidence.

scanning of those parameters not included in the ANOVA study show even less variation over time than those studied (for example, fluoride ion and total hardness, Appendix 1), and thus are even less likely to indicate any differences between the output of the plants. However the point should be made that the two plants draw raw water from the same source (the North Saskatchewan River) and utilize essentially the same steps in the water treatment process. Therefore it is not altogether surprising that the observed results were obtained, unless the differences in intake location had an effect. Note, however that none of the samples analyzed during this study were obtained during urban runoff periods (see page 44), so the conclusions drawn do not take into account the effect of storm sewer and other urban runoff upon the water entering the Rossdale plants.

As a final observation it can be stated that the Edmonton water treatment plants appear to be providing good statistical control over the characteristics and overall quality of the water entering the distribution system under normal conditions.

1.5.3 Pipe Materials Study

Materials used for the construction of distribution pipes should possess the following characteristics[29];

(a) Excellent tensile and bending strength to withstand external loads resulting from trench backfill and earth movement caused by freezing, thawing, and unstable soil conditions.

(b) High bursting strength to withstand internal water pressures, along with the ability to resist impact loads which may occur during transportation, handling, or installation.

(c) A smooth and non corrosive interior surface, and an exterior surface which remains essentially unaffected by aggressive soil and groundwater.

(d) The capability of being provided with tight joints and easily tapped for good connections.

The Edmonton water distribution system consists of approximately 2600 km of piping of various diameters. These pipes are constructed from three major types of material. The first, cast iron, was mostly laid down in the early part of this century and is mainly present now in the older parts of the city in the "downtown" core. The second major type of material, asbestos cement, was used for much of the piping laid down in the middle of this century in suburban areas. The last of the materials, polyvinyl chloride (PVC), is now the material of choice for distribution system pipes due to its high tensile strength and resistance to corrosion. A major program was begun in the early 1970's to replace all cast iron piping (some 1100 km) with PVC. This is necessary because the cast iron pipes have become brittle and corroded with age and are the cause of the majority of main breaks now occuring in the system. It is expected the replacement program will not be completed until the early part of the next century. In addition to these three materials small amounts of other materials are present in the system, including some stainless steel piping.

In addition to external corrosion another potential problem in distribution pipe is the build-up of deposits on the inner walls of substances such as calcium carbonate ($CaCO_3$) and aluminium oxides[22]. The most common of these materials is calcium carbonate, which under extreme conditions can accumulate in sufficient quantities to virtually seal off a pipe. Some deposition is beneficial, however, for an evenly deposited layer acts an an internal barrier to corrosion and prevents contamination of water in the pipes by materials such as lead and organic compounds that may leach from plastic piping over time. Thus it is important to maintain some control over the amount of precipitation taking place in the system.

The Langelier saturation index[30,31], SI, is a measure of the ability of a water to deposit or dissolve the calcium carbonate coated on a pipe. It is defined by the equation;

$$SI = \log_{10} ([H_s^+] / [H^+])$$

where

SI = The Langelier saturation index.

$[H_s^+]$ = hydrogen ion activity at calcium carbonate saturation.

$[H^+]$ = actual hydrogen ion activity of the water.

This equation has been modified by several authors to enable the SI to be calculated in terms of common water parameters.

A variation on SI is the concept of aggressiveness index, used to determine the optimum pH range at which deposition occurs to an acceptable degree. The aggressiveness index, AI, is given by;

$$AI = pH + \log_{10} (TH)$$

where

T = the total alkalinity (in mg/L as $CaCO_3$).

H = the calcium hardness (in mg/L as $CaCO_3$).

Aggressive water strips calcium carbonate deposits from pipe walls while non-aggressive water allows deposits to build up. Hence it is necessary to find a compromise between these two extremes. A comparison can be made between the SI and AI as follows;

	AI	SI
Highly aggressive water	10.0	-2.0
Moderately aggressive water	10.0 to 11.9	-2.0 to -0.01
Non aggressive water	12.0	0

Practical experience in the Edmonton system indicates that aggressiveness index should be kept above 11.5. This corresponds to an optimum pH range in the system of 8.2-8.5.

During this study of pipe materials several problems were encountered in addition to that of deposited material "masking" the nature of the pipe surface. The major problem was that as the water travels from the treatment plant to the sampling site it often passes through pipes of different materials. Hence it may be virtually impossible to determine the effects different materials would have on the quality of the water flowing through the pipe. However, it was possible to do a limited study based on areas of the city where one type of pipe material predominates. In addition we were able to get access to detailed cadastral maps of the city. Cadastral maps are plans produced for the City water engineering branch that provide detailed information on construction materials and dimensions of the water and sewage pipes, as well as related information such as the locations of fire hydrants. Hence it was possible to obtain a substantial amount of information on the nature of the pipe materials near the sampling locations used during this work prior to the study.

To see whether any statistical differences in water quality could be detected based on pipe materials a second ANOVA study was carried out. Three parameters, chloramines, turbidity, and organic carbon, were used to compare the water quality at several sites in the cast iron mains area with a similar number in the asbestos cement mains area. The period of time covered by the ANOVA study was from September 1988 to February 1989. The selected sites (number of sites in parentheses) were as follows:

(a) Cast iron mains area (8): North Jasper Place, Clareview, Londonderry, and Rosslyn #1 reservoirs along with fire halls #1, #3, #6, and #10.

b) Asbestos cement area (8): Thorncliff, Ormsby, Kaskitayo, and Castledowns reservoirs along with fire halls #17, #19, #20, and #23.

The results of the ANOVA tests (Table 1.5) provide no evidence that the nature of the pipe material has any detrimental effect on water quality insofar as the three parameters studied are concerned. It appears likely that once a calcium carbonate coating has formed the original pipe material no longer affects water quality. Problems are most likely to occur when the pipe is new and leaching of organics or other materials into the water may occur; this has been reported[9-12].

1.5.4 Dead-End Location Study

Dead-end locations[7,8] are regions where circulation in the mains is curtailed. They primarily occur at the outer edges of the distribution system and are often a source of customer complaints of poor water quality. These locations are usually found in cul-de-sacs, in areas where there are only one or two houses at the end of a main, or in areas of new housing construction. In the City of Edmonton distribution system dead-ends are relatively uncommon because the majority of mains are built using a "looped" design to effectively eliminate standing water. For customers who live in known dead-end locations guidelines are issued which are designed to minimize problems with water quality which occasionaly arise.

Several possible dead-end mains were identified by the City of Edmonton engineering branch when a pipe cleaning program[32] was initiated in the fall of 1988. One of these sites, together with another near a new housing development, were monitored by taking several samples (at random) from private houses in these two locations over a period of several months. The data obtained during this study is shown in Tables 1.6 and 1.7.

Table 1.5

Summary of ANOVA Results for the Pipe Material Study.

(a) Reservoirs

Parameter	Study Duration	F calcd	F table (1)	F table (2)
Total Chloramines	September-February	3.89	4.08	7.31
Turbidity	September-February	0.12	4.08	7.31
Organic Carbon	September-February	1.47	4.08	7.31

(1) At the 95 % level of confidence

(2) At the 99 % level of confidence

(b) Fire Halls

Parameter	Study Duration	F calcd	F table (1)	F table (2)
Total Chloramines	September-February	0.24	4.08	7.31
Turbidity	September-February	3.08	4.08	7.31
Organic Carbon	September-February	3.78	4.08	7.31

(1) At the 95 % level of confidence

(2) At the 99 % level of confidence

Table 1.6

Data Collected From "dead end" Mains Sampling Locations.

(1) 189th Street and 92nd Avenue

(a) Non Metals (Residuals)

Date Sampled	Total Chloramines	Total Oxid	F^- ion	pH	Turbidity	Total Hard	Ca Hard	Total Alk	Org Carb
	ppm	ppm	ppm		NTU	ppm	ppm	ppm	HAU
11/9/88	1.91	0.28	0.93	8.3	0.15	104	70	52	3.35
18/10/88	1.84	0.26	1.02	8.5	0.20	114	62	60	3.57
16/12/88	1.86	0.27	0.97	8.5	0.15	110	64	60	2.49
12/1/89	1.79	0.22	1.01	8.3	0.35	116	60	59	3.29
22/2/89	1.87	0.23	0.95	8.5	0.10	113	60	51	3.45
18/3 89	1.86	0.24	1.00	8.2	0.20	115	64	56	3.08
19/4/89	1.74	0.28	0.96	8.2	0.45	111	77	44	7.81

(b) Metals

Date Sampled	Aluminium	Cadmium	Chromium	Copper	Iron	Lead
	ppb	ppb	ppb	ppb	ppb	ppb
11/9/88	380	0.3	0.4	17	1	0.7
18/10/88	320	0.1	0.6	11	2	0.8
16/12/88	410	0.1	0.6	9	4	0.9
12/1/89	460	0.1	0.5	6	3	0.8
22/2/89	290	0.1	0.7	7	4	1.0
18/3 89	300	0.1	0.6	4	5	0.8
19/4/89	320	0.1	0.4	6	12	0.7

Table 1.7

Data Collected from "dead end" Mains Sampling Locations.

(2) 110 th Street and 158 th Avenue

(a) Non Metals (Residuals)

Date Sampled	Total Chlora -mines	Total Oxid	F^- ion	pH	Turbid ity	Total Hard	Ca Hard	Total Alk	Org Carb
	ppm	ppm	ppm		NTU	ppm	ppm	ppm	HAU
11/9/88	1.99	0.25	0.93	8.4	0.40	109	70	52	3.48
22/10/88	1.84	0.30	0.94	8.4	0.10	113	66	55	2.51
17/11/88	1.77	0.26	1.00	8.4	0.15	107	68	59	1.99
1/12/88	1.85	0.22	0.93	8.2	0.20	115	66	53	3.03
19/2/89	1.89	0.29	0.96	8.3	0.15	112	66	50	3.89
18/3 89	1.77	0.27	0.98	8.3	0.25	112	74	45	3.60
10/4/89	1.75	0.29	0.97	8.3	0.40	112	76	44	6.51

(b) Metals

Date Sampled	Aluminium	Cadmium	Chromium	Copper	Iron	Lead
	ppb	ppb	ppb	ppb	ppb	ppb
11/9/88	420	0.3	0.4	2	2	0.8
22/10/88	340	0.1	0.5	1	2	0.9
17/11/88	370	0.2	0.6	3	4	0.9
1/12/88	390	0.1	0.5	2	3	0.9
19/2/89	300	0.1	0.6	3	5	1.1
18/3 89	320	0.1	0.5	3	2	0.7
10/4/89	330	0.1	0.4	7	10	0.6

The data indicates that the measured parameters are within normally accepted limits for distribution system samples. Several samples from both sites have slightly low total chloramine levels, but not sufficiently low to be considered significant. Levels of copper at the 92nd Avenue site are slightly higher than normal and may possibly be due to leaching from domestic copper piping. Aside from these observations there appears to be sufficient flow of water in the pipes to maintain adequate water turnover and maintain the water quality. Because problems can occur when water is allowed to stand in the mains over a period of time, customers in dead-end areas are advised to allow water from a tap to run for a time in the morning to clear the lines. In general, dead end problems affect only a small number of customers in the city.

1.5.5 Spring Runoff Study (April 1989)

Spring runoff periods in Edmonton can be classified into two categories i.e urban and rural. The former (which occurs earlier) is a result of organic material accumulated in the storm sewers and other urban sites being washed into the river during the spring thaw. The latter is produced by the release of organic material from decaying vegetation and other materials into the river from upstream as the snow melts during the spring. During runoff periods the water may acquire unpleasant taste and odor characteristics which the normal treatment process cannot entirely eliminate, this is reflected by the high number of customer complaints which are received during runoff periods.

During an extended period of rural runoff which occurred in Edmonton in April 1989 some variations in several of the water parameters studied in this work were observed, notably soluble organic carbon, copper, iron, and to a lesser extent turbidity. A number of additional samples were collected from the fire halls during this time; the results of analyses for selected parameters are shown in Table 1.8.

Table 1.8

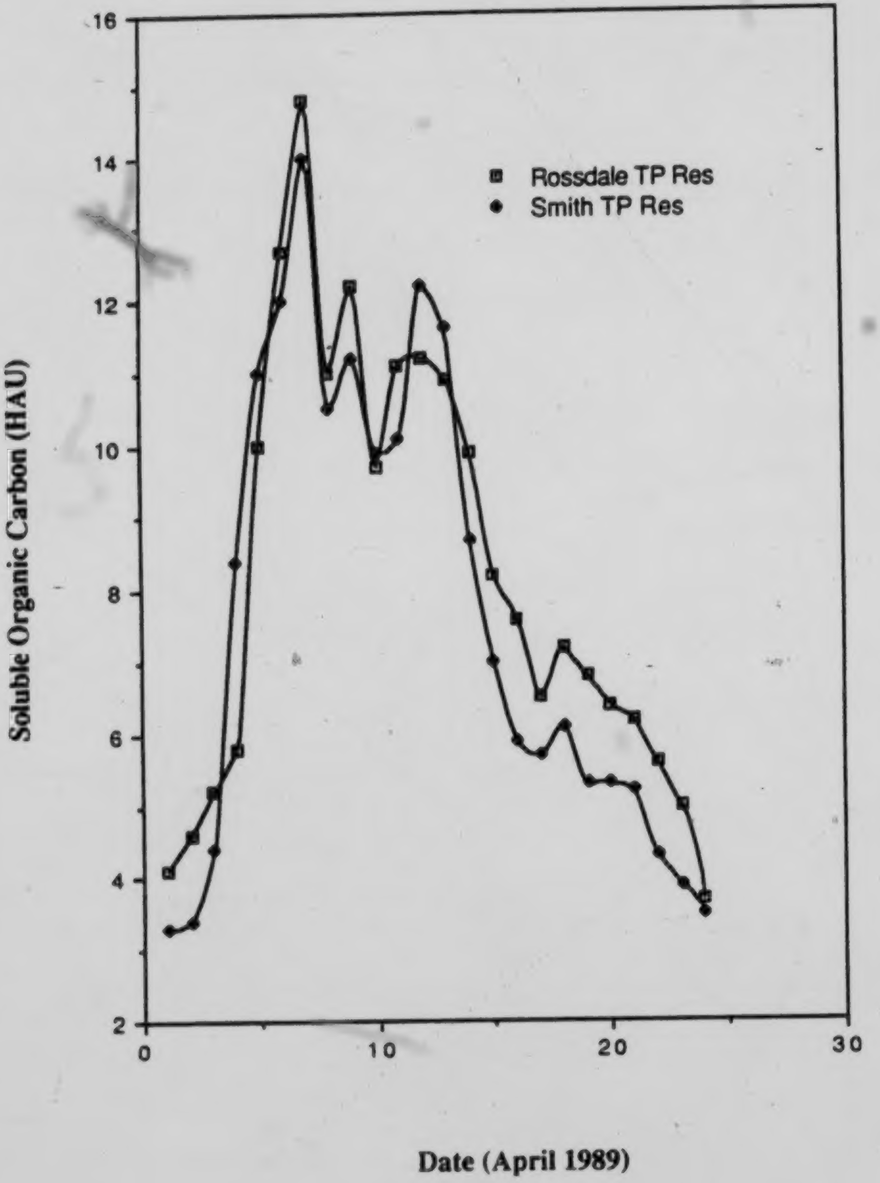
Results of Analyses of Additional Samples Collected From City of Edmonton Fire Halls During Spring Runoff, April 1989.

Fire Hall	Sampling Date	Organic Carbon	Iron	Copper
		HAU	ppb	ppb
# 1	7 th	12.28	6	3
# 2	7 th	12.62	4	3
# 3	6 th	11.27	40*	12
# 4	10 th	10.25	5	3
# 5	7 th	12.58	6	5
# 6	7 th	11.76	8	15
# 7	8 th	11.47	9	2
# 8	11 th	9.95	14	9
# 9	13 th	10.82	12	12
# 10	7 th	9.67	9	2
# 11	8 th	12.51	50*	2
# 12	7 th	11.45	7	12
# 13	8 th	8.78	17	3
# 15	8 th	11.33	20	14
# 16	8 th	8.76	11	11
# 17	11 th	10.40	4	8
# 19	7 th	11.47	9	8
# 20	8 th	11.39	4	8
# 22	7 th	12.70	13	2
# 23	10 th	10.53	50*	10
# 24	10 th	11.54	5	9

* Original sample was diluted x10 prior to analysis

Figure 1.7

Levels of Soluble Organic Carbon as Determined by UV Measurement in Rossdale and E.L.Smith Water Treatment Plant Reservoirs During Spring Runoff, April 1989.



The measurement of absorbance at 200 nm[26] is perhaps the best indicator of the onset of rural runoff (it has been shown[6] that many of the compounds present at trace levels in urban runoff do not absorb at this wavelength therefore this method is not useful for the determination of the onset of urban runoff periods) because it provides a relative indication of the presence of increasing amounts of organic material (particularly humic material) in the water. A good illustration of this is shown in Figure 1.7, which shows the organic carbon levels in the two treatment plant reservoirs present during April 1989. The plots show the appearance of increasing levels of organic material in the water at the beginning of the month, with a maximum around the 6 th and a gradual return to normal levels (2-4 HAU) by the end of the month. This general trend was also observed in samples collected from the distribution system during this same period (see Table 1.8).

Increased levels of copper and iron were also observed during this time in samples collected from the distribution system. One reason for these increases may be the higher doses of chemicals used in the treatment process, since trace levels of copper and iron are present in some of the chemicals used in the process. Another reason may be that the metals are coming from the raw river water itself. Previous studies on the North Saskatchewan River[2,33] have shown some seasonal variations in the levels of a number of metals, but data on the raw water are not plentiful.

Copper and iron, as well as other metals such as lead, can form soluble complexes with fulvic and humic acids[34-38] and their derivatives, which form a major part of the organic matter present in the river water during runoff. The structure of these complexes are exceedingly complicated, but they appear to have the potential to form relatively stable metal complexes. It is possible that the observed increase in the levels of these metals is due to the formation of these complexes (either in the raw water or in the treatment processs) which then enter the distribution system intact.

Of the possibilities cited above, the most likely explanation is that the additional metals come from the extra bulk chemicals used in the treatment process. Samples collected from the distribution system after the runoff showed essentially normal levels of iron, and copper. The possibility of complex formation remains, however, and deserves more detailed study at some future time.

1.6.1. Conclusions and Suggestions for Further Work

The data obtained during the course of this study indicate that the overall quality of the drinking water in the City of Edmonton distribution system appears excellent. Little variation in the water quality was observed over the year, with the exception of a short period in April 1989 during spring runoff. The treatment plants appear to maintain tight control over the level of the water parameters measured in this work and the treatment process itself appears to be in a state of statistical control.

As regards a sampling program for the distribution system, several conclusions can be drawn from this study. First, the total number of sites (34) utilized as primary sampling locations in this study appeared to provide sufficient coverage of the distribution system and were in addition readily accessible for sample collection. The utilization of more distribution system sampling sites would probably not provide significantly more information on the water quality in the system and would result in site duplication. An exception is the monitoring of potential trouble spots such as "dead ends", where additional sampling sites may be required.

Samples should be collected from the system at a frequency such that any problem with water quality can be detected in time for appropriate remedial action. For routine monitoring of the Edmonton distribution system a sampling frequency of one or two per month from each reservoir and one per month from each of the fire halls appears to be sufficient. All parameters (including metals) should be determined in these samples. Sampling frequency should be increased where the water quality in the distribution system is undergoing changes, such as during runoff or in localized areas. Since the water produced in the treatment plants is monitored before it enters the distribution system, a good "snapshot" of the water quality in the distribution system is provided. In this regard, it should be noted that with the exception of the spring runoff period in April 1989, the system was not subject to any significant perturbations, and so the conclusions are based on relatively stable operating conditions.

As for the analytical procedures for the measurement of the parameters monitored during this study, there appear to be few problems. More determinations of metals should probably be carried out, especially on the bulk chemicals used in the treatment process. The question of how much trace metals in the bulk treatment chemicals contribute to the overall concentration of metals in the water is unclear and warrants further study.

Overall, from this comprehensive study on the quality of the drinking water in the City of Edmonton distribution system over a one year period, it can be concluded that the quality is excellent, and no major variations were observed. This data set can be used as a reference should it be decided to do a similar study at some time in the future.

Chapter 2

The Determination of Chlorine Dioxide in Drinking Water

2.1.1 General

One important commercial use of chlorine dioxide (ClO_2) is as a disinfectant in the water treatment industry. Chlorine dioxide is one of several compounds (along with ozone and chloramines) that are usually referred to as "alternative disinfectants". The search for disinfectants to replace chlorine, which has been used since the turn of the century, intensified when it was discovered in 1974[39] that the reaction of chlorine with certain organic compounds when present at trace levels in drinking water led to the formation of potentially carcinogenic trihalomethane (THM) compounds[40-42]. In recent years the commercialization of these alternative disinfectants has increased dramatically and nowadays they are used virtually worldwide to disinfect municipal drinking water supplies.

2.2.1 Ideal Disinfectant Characteristics

Disinfection itself is a specialized treatment for the destruction of waterborne bacteria and viruses that are potentially harmful to man. An "ideal" disinfectant species for use in water treatment must fulfil a number of criteria[43]. These are summarized as follows:

(a) It must have the ability to destroy organisms present within the available contact time[44] , the range of water temperatures encountered, and the anticipated fluctuations in composition, concentration, and condition of the water being treated.

(b) It should be capable of being easily and safely generated and should be cost effective.

(c) It should have the ability to achieve the desired objectives without the production of potentially toxic by-products.

(d) It should persist in sufficient residual concentrations to prevent recontamination of the water at a later date. Analytical methodology should also be available to accurately determine this residual for process control, and as a measure of disinfection efficiency.

In practice no single disinfectant species meets all these criteria. Therefore certain compromises are necessary to achieve optimum disinfection. This often means use of a combination of disinfectants, such as chloramines and chlorine dioxide, to achieve the desired results.

Chlorine Dioxide as a Disinfectant

2.3.1 History

Chlorine dioxide was first discovered in 1811 by the British scientist Sir Humphrey Davy (who is also credited with the invention of the coalminers helmet lamp). He called the green-yellow gas euchlorine[45], and produced it by acidifying potassium chlorate ($KClO_3$) with sulfuric acid. In 1940 Taylor and co-workers[46] reported on the superior bleaching characteristics of sodium chlorite ($NaClO_2$), and in the same paper also discussed the production of chlorine dioxide gas from sodium chlorite on acidification or reaction with chlorine. These reactions provided a means to generate chlorine dioxide on a commercial basis, and led to the first reported use of chlorine dioxide in water treatment in 1944 at the Niagara Falls, N.Y., water treatment plant[47]. Since then the use of chlorine dioxide has gained in popularity and it is estimated that several thousand utilities in Europe and 300 to 400 in North America now use chlorine dioxide for disinfection purposes. This number is expected to increase rapidly over the next decade.

2.3.2 Advantages and Disadvantages

Chlorine dioxide as a disinfectant has many of the desirable properties listed earlier. It is recognized to be a powerful bactericide[48,49] and viricide[50], although its exact mode of action is somewhat unclear. It is most effective over the pH range 6.5 to 8.5, which is the range normally encountered in water treatment. Another advantage is that chlorine dioxide does not promote the formation of THM compounds[51,52]. In addition, it rapidly oxidizes phenolic compounds[53] which are thought to contribute to taste and odor problems in the city drinking water[90] during runoff periods. Finally, the equipment required to generate chlorine dioxide is relatively easy and inexpensive to maintain once the original capital outlay has been made. Overall chlorine dioxide is quite cost effective.

The use of chlorine dioxide has, however, several major disadvantages. For example it does not persist to any extent in the distribution system, but is converted to chlorite ion (ClO_2^-), chlorate ion (ClO_3^-) and chloride ion (Cl^-)[54]. Most of the chlorite ion slowly degrades by undergoing reactions with oxidizable material in the finished water, but some remains unreacted. In recent years serious concern have been raised about the possible toxicity of both chlorite ion and chlorate ion . A number of studies have been done on the potential health risks associated with these species; an excellent review of these studies can be found in reference 55. Because chlorine dioxide does not persist, chloramines are often used in combination with chlorine dioxide as a secondary disinfectant to ensure that sufficient residual is maintained in distribution systems to prevent possible re-infection. Other disadvantages of chlorine dioxide are that it has also been associated with possible taste and odor problems[127] in drinking water and the analytical methodology to measure trace levels of chlorine dioxide in water is somewhat limited. This will be discussed in detail later in this chapter.

2.3 3 Physical and Chemical Properties of Chlorine Dioxide

Chlorine dioxide (molecular weight 67.46) is one of the few compounds in nature that is thought to exist almost entirely as a monomeric free radical[54]. Liquid chlorine dioxide is deep red in color and is highly explosive above -40° C. In the vapor phase it closely resembles chlorine in both appearance and odor. Concentrated chlorine dioxide vapor is also explosive at 5.8 psi (40 kPa) above normal atmospheric pressure, and all attempts to compress or store chlorine dioxide gas either alone or in combination with other gases have been commercially unsuccessful. Because of the explosion hazard chlorine dioxide must be generated at the point of use. Solution concentrations below about 10 g/L do not produce a sufficiently high vapor pressure to present an explosive hazard and since solutions of the order of 1-4 g/L are the highest usually encountered in water treatment their use can be considered safe. Chlorine dioxide is extremely soluble in water, in which it forms a green-yellow solution and, unlike chlorine does not hydrolyze to any great extent. It remains stable as a dissolved gas in solution over a relatively wide range of pH (from 2 to 10).

The inorganic[56] and organic[56,57] chemistry of chlorine dioxide has been extensively studied and several excellent review articles are available[56,58]. In this thesis relevant aspects of chlorine dioxide chemistry will be discussed, but for more detailed discussion the reader is referred to the review articles mentioned above.

2.3.4 Generation of Chlorine Dioxide

All chlorine dioxide for water treatment is generated *in situ* from sodium chlorite. Most generative techniques use the oxidative process in which chlorine, either as a gas or in solution, is mixed with sodium chlorite in solution[54]. The stoichiometry of the reaction for molecular chlorine is:

$$2\,NaClO_2 + Cl_2 = 2\,ClO_2 + 2\,NaCl \quad (1)$$

In addition to the formation of the desired chlorine dioxide, chlorate ion may also be formed as a by-product by the following side reaction:

$$NaClO_2 + Cl_2 + OH^- = NaClO_3 + HCl + Cl^- \quad (2)$$

The goal in generating chlorine dioxide from chlorine and sodium chlorite is to maximize the yield, which is defined as the molar ratio of chlorine dioxide produced to the sodium chlorite used, to the theoretical maximum. The term "conversion" is also used in this context and is defined as the molar ratio of the amount of chlorine dioxide formed to the amount of sodium chlorite fed to the system. For equation (1) the terms yield and conversion have the same meaning.

Studies on the mechanism[56] and kinetics[59,60] of the chlorine-sodium chlorite reaction have shown that conditions favouring the optimum formation of chlorine dioxide are those in which the reactants are present in high concentration and the chlorine is present either as hypochlorous acid (HOCl) or molecular chlorine (Cl_2). The use of these two species keeps the pH of the system low and therefore minimizes reaction (2). Two commercially available systems exist for the generation of chlorine dioxide. These are the aqeuous chlorine-sodium chlorite system and the gaseous chlorine-sodium chlorite system. The latter system (Rio Linda Chemical Co, Rio Linda, Cal) is installed in the Edmonton water treatment plants. A schematic of this system is shown in Figure 2.1.

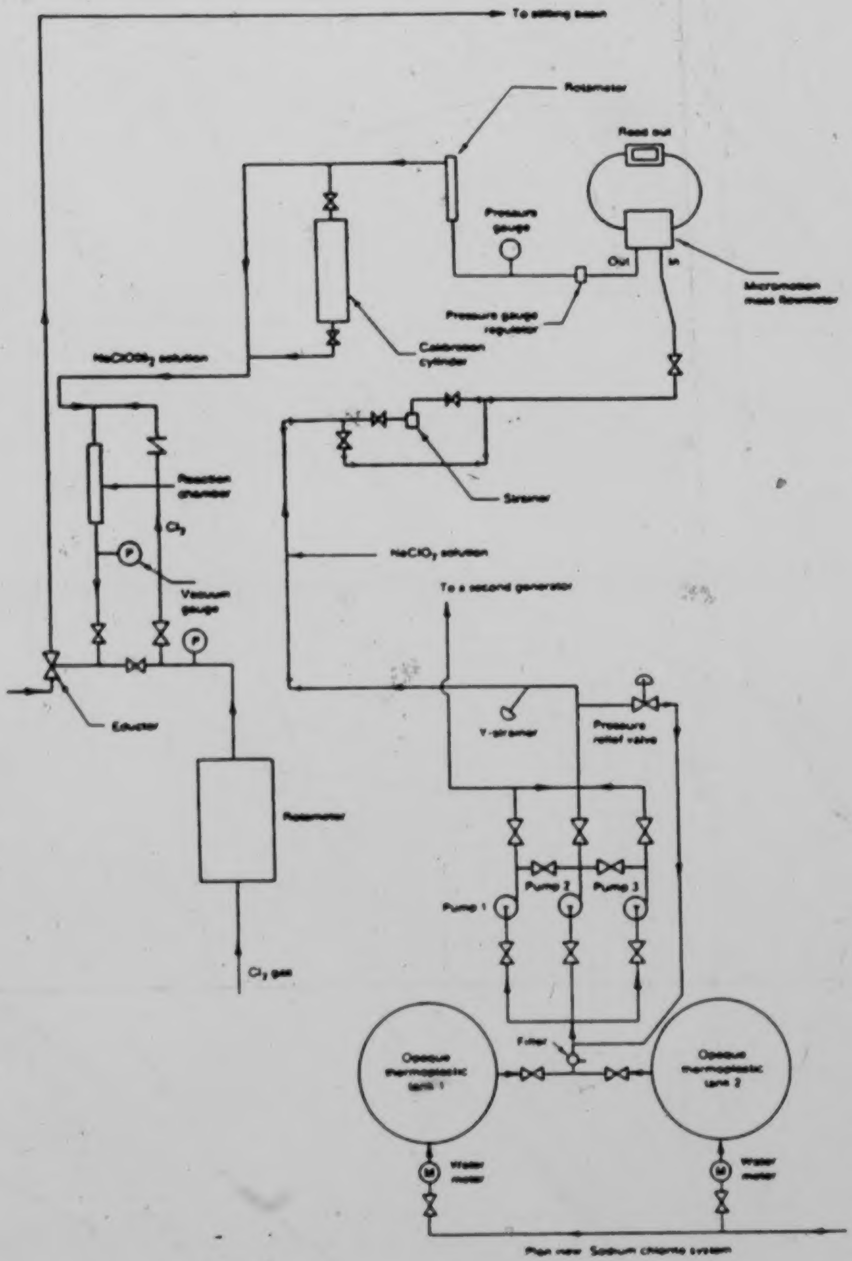
The Determination of Chlorine Dioxide (A Literature Review)

2.4.1 Introduction

Although several methods have been proposed for the determination of chlorine dioxide, none can be considered ideal. Hence the search for more sensitive methods continues as the use of chlorine dioxide becomes more widespread. Of the methods currently available few are direct, and so they have to be compared with a "referee method" to ensure accurate data. These "referee methods" also have limitations. In this review the various methods now available for the determination of chlorine dioxide

Figure 2.1

Schematic Diagram of the Rio Linda Chlorine Dioxide Generating Unit Installed at the Rossdale and E.L.Smith Water Treatment Plants.


To settling basin
Rotameter
Read out
Pressure gauge
Out
In
Micromotion mass flowmeter
Pressure gauge regulator
Calibration cylinder
NaClO2 solution
Reaction chamber
Cl2
P
Vacuum gauge
P
Strainer
NaClO2 solution
To a second generator
Eductor
Y-strainer
Pressure relief valve
Rotameter
Pump 1
Pump 2
Pump 3
Cl2 gas
Filter
Opaque thermoplastic tank 1
Opaque thermoplastic tank 2
M
Water meter
M
Water meter
Plan view Sodium chlorite system

in drinking water will be discussed. Specific details such as the working range and estimations of the detection limits will be given whenever possible. Particular attention will be paid to interferences for each method because many of them are prone to serious interferences from a number of species.

2.4.2 Iodometric Titration Method

The principle of this Standard Method[16] is based on the reaction between chlorine dioxide and potassium iodide[61], and forms the basis of several methods for the analysis of chlorine dioxide (see, for example, the section on amperometric titrations). Iodide ion is oxidized by chlorine dioxide in the presence of acids such as acetic or sulfuric acid to form iodine. The liberated iodine is then titrated with standard sodium thiosulfate ($Na_2S_2O_3$) to a starch indicator end point.

The working range for this method is up to 10 mg/L as chlorine dioxide with a reported detection limit of 20 μg/L. Possible errors in the method[62] include air oxidation of iodide ion, and contamination of the iodide solution by iodate (IO_3^-). In addition chlorine, chlorite ion, chloramines, and several metal ions, including Fe^{3+}, are potential interferents because the procedure is unable to distinguish among them. Therefore we can say that although the iodometric method may provide a "referee method" for the standardization of pure solutions of chlorine dioxide, it is not satisfactory for real samples where a number of potential interferences to the method are likely to exist.

2.4.3 Amperometric Titration Methods

Two amperometric titration methods for the analysis of chlorine dioxide are listed in the most recent edition of Standard Methods[63]. They are to some extent extensions based on the amperometric titration of chlorine and chloramines (see Chapter 1) which is regarded as the water industry standard method for those species, and are discussed here as methods 1 and 2.

Method 1[64]

In this method four separate titrations with phenylarsine oxide (PAO) are carried out on individual aliquots of the sample to determine sequentially the concentrations of free chlorine (which includes hypochlorous acid (HOCl) and hypochlorite (OCl^-)), chloramines, chlorite ion, and chlorine dioxide. In the first titration the pH is raised to 12 with 6M sodium hydroxide to decompose all the chlorine dioxide that may be present in the sample. The solution is then neutralized by the addition of 6M sulfuric acid and titrated with PAO to determine free chlorine. A second portion of sample is treated in a similar way, but 1 mL of 2M KI solution is added after the solution has been adjusted from pH 12 to pH 7. The portion is then titrated with PAO to determine free chlorine and chloramines. The third sample is directly adjusted to pH 7 by the addition of phosphate buffer and KI is added prior to titration. This titration determines free chlorine, chloramines, and one fifth of the chlorine dioxide. To the fourth sample KI is added and the pH lowered to 2 by the addition of 6M H_2SO_4. The pH of the sample is then raised to 7 by the addition of 6M NaOH and titrated to determine all four species: free chlorine, chloramines, chlorite ion, and chlorine dioxide. The individual titration volumes are then converted into concentrations of the various species in the sample.

A number of potential problems have been identified in this procedure. For example, it has been shown[65] that in the first two titrations, a pH of 12 may be insufficient to decompose fully all the chlorine dioxide in the sample. If the ClO_2 is not removed it will interfere, particularly in the second titration where it will react with KI to liberate iodine (I_2) and will thus be titrated. Another source of error can arise if the concentrated acid and base is not added slowly and with good mixing. During addition of acid, chlorite ion may react to form more chlorine dioxide. Also, iodide may be oxidized to iodine by dissolved oxygen in strongly acidic solutions by the reaction:

$$4\,I^- + 4\,H^+ + O_2 = 2\,I_2 + 2\,H_2O$$

Possible interferents in the method are nitrogen trichloride (NCl_3), free halogens, and copper. Most common metals such as manganese and iron do not interfere. Although this method is still currently used as a "referee method" for the analysis of chlorine dioxide it is long and laborious. In addition, since concentrations are determined by difference, it is potentially inaccurate.

Method 2

A second amperometric titration procedure was reported by Aieta and co-workers[66]. It is essentially a modification to the one already outlined. Like the previous method a succession of amperometric titrations are employed to determine the concentrations of various chlorine species in solution. The procedure is based on the fact that equilibria for the reduction of chlorine species by iodide are pH dependent. Sodium thiosulfate is used as titrant instead of PAO and there are several other differences in procedure from the previous method.

The Aieta method can be used to determine both free and combined chlorine (but cannot differentiate between the two), chlorite ion, and chlorine dioxide in four successive titrations. In the first an aliquot of sample is adjusted to pH 7 with phosphate buffer. Solid KI (0.5 to 1g) is then added and the sample titrated with thiosulfate to an amperometric end point. In this step chlorine and one fifth of the chlorine dioxide are determined according to the equations:

$$Cl_2 + 2\,I^- = I_2 + 2\,Cl^- \quad (1)$$

$$2\,ClO_2 + 2\,I^- = I_2 + 2\,ClO_2^- \quad (2)$$

$$I_2 + 2\,S_2O_3^{2-} = 2\,I^- + S_4O_6^{2-} \quad (3)$$

In the second step the pH of the sample from the previous step is lowered after titration to 2 and again titrated after the addition of solid KI. This step determines the remaining chlorine dioxide and all the chlorite ion present in the sample according to:

$$2\,ClO_2 + 10\,I^- + 8\,H^+ = 5\,I_2 + 2\,Cl^- + 4\,H_2O \quad (4)$$

The I_2 is titrated with thiosulfate as before.

In the third step a second aliquot of sample is buffered at pH 7, then placed in a specially designed gas wash bottle and purged with nitrogen to remove all chlorine dioxide from solution. After purging, KI is added and the sample again titrated to determine any chlorine that remains (equation 1).

In the final step the pH of the purged sample from step 3 is lowered to 2 with 6M hydrochloric acid, KI is added and the sample titrated. In this step chlorite ion alone is determined. Since all chlorine dioxide has been removed in the purging step, the chlorite ion determined is only that present in the original sample; thus the concentration of chlorine dioxide can be determined by subtraction. The relevant equation for step 4 is:

$$ClO_2^- + 4\,I^- + 4H^+ = 2\,I_2 + Cl^- + 2\,H_2O \quad (5)$$

Once all the titrations have been carried out the various titration values obtained can be converted to concentrations according to known formulae. Note that this method was chosen as a referee method for the work described later in this study. Details of the calculations involved in determining the various species as well as a description of the apparatus is provided in the experimental section.

The detection limit for chlorine dioxide using this method has been reported as 0.045 mg/L in treated drinking water. The working range of the method is large, making it useful for determining the yield of chlorine dioxide generating systems.

Potential problems with the method include the possibility of oxidation of iodide by dissolved oxygen in acidic solutions (see method 1), and possible iodate (IO_3^-) formation above pH 4. Species reported to be interferents for this method include manganese, copper, and nitrite (NO_2^-). No attempt has been reported to determine the extent of these interferences.

Despite the fact that in this method results are obtained by difference and the procedure is relatively lengthy, it is considerably less prone to error than either of the methods previously outlined. For these reasons this method was selected as a referee method for this study.

2.4.4 UV Spectrophotometry

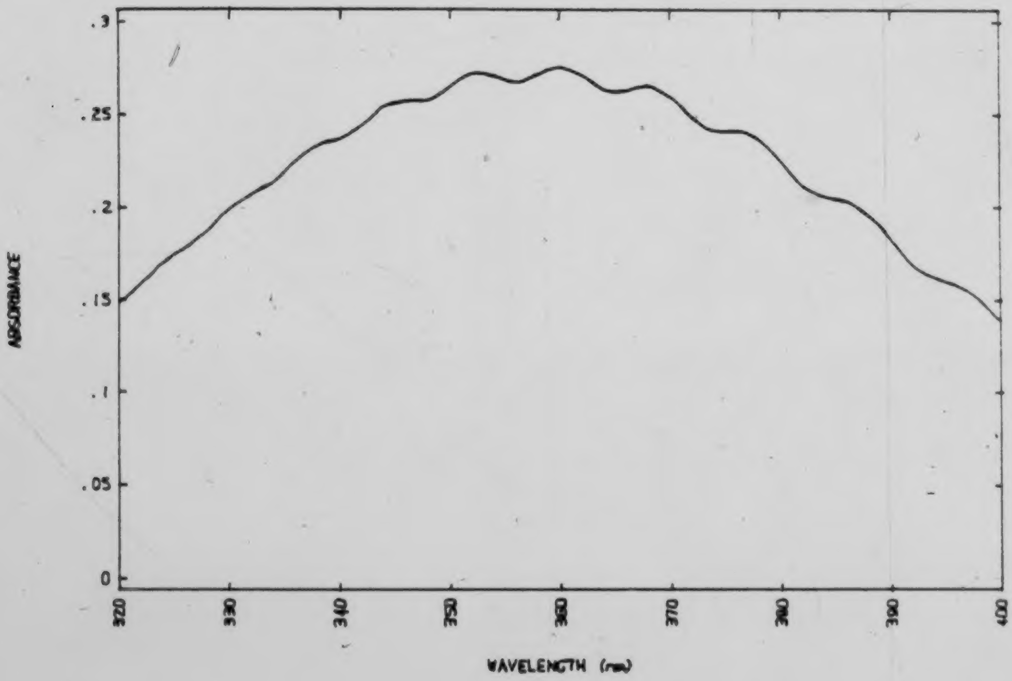
Chlorine dioxide has a characteristic absorbance spectrum (Figure 2.2) in the UV/visible region from 340 to 390 nm. The maximum absorbance is at 360 nm with a molar absorptivity[56] of 1250 M^{-1} cm^{-1}. The sensitivity of spectrophotometric analysis is limited by molar absorptivity, and the detection limit is dictated by a combination of molar absorptivity and the path length of the measurement cell. Although other absorbers at this wavelength seriously interfere with the method in real samples, the UV method has often been used as a referee method for the standardization of pure chlorine dioxide solutions. Gordon has reported[62,67] a detection limit of 0.05 mg/L for this method and estimated a working range from 0.05 to 500 mg/L. Because of its simplicity, large potential working range, and the fact that it is one of the few direct methods of analysis available for chlorine dioxide, this method was selected as a second referee method for this study.

2.4.5 Colorimetric Methods

A number of colorimetric methods have been developed for the analysis of chlorine dioxide. All are indirect and require a referee method for standardization. The majority

Figure 2.2

Ultraviolet-Visible Spectrum from 320 to 400 nm of an Approximately 15 mg/L Solution of Chlorine Dioxide, Recorded on an HP 8451 Diode Arrray Spectrophotometer in a 1-cm Path Length Cell.



have poor selectivity, which has precluded their use in the routine analysis of real samples. Structures of several of the more common colorimetric reagents that have been applied to the determination of chlorine dioxide are shown in Figure 2.3.

2.4.5.1 N,N-Diethyl-p-phenylenediamine (DPD)

This method, originally developed for the determination of chlorine, has been extended to the determination of chlorine dioxide[68,69]. It can be used either as a titration or a colorimetric method. As in the amperometric methods discussed earlier, several chlorine species may be determined sequentially by a series of titrations or spectrophotometric measurements and their concentrations determined by difference. For the determination of chlorine dioxide, the initial step in the sequence is sufficient. Only one fifth of the total chlorine dioxide is determined.

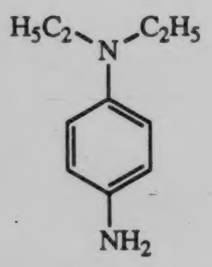
To a 100-mL aliquot of sample, 2 mL of glycine solution (prepared by dissolving 10g of glycine in 100 mL of distilled water) is added and the solution is mixed. Aliquots (5-mL each) of phosphate buffer (pH 6.2 to 6.5) and DPD reagent solution (prepared by dissolving 1g of DPD oxalate and 200 mg EDTA in 1 litre of distilled water containing 8 mL of 12M sulfuric acid) are taken and mixed in a separate flask. The contents of the two flasks are then combined to produce a red solution. The absorbance obtained is measured by using either a spectrophotometer at 515 or 550 nm or a visual color comparator. The absorbance is related to concentration by use of a standard calibration curve.

The reported detection limit for chlorine dioxide using this method is 0.008 mg/L[69] with a working range of 0.008 to 20 mg/L. The method has, however, a number of problems associated with it. One is that it does not differentiate between chlorine dioxide and chlorite. Another is that a number of species can interfere with the method,

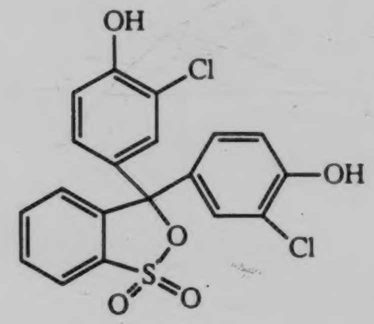
Figure 2.3

Chemical Structures of Four Colorimetric Reagents That Have Been Used for the Analysis of Chlorine Dioxide in Water.

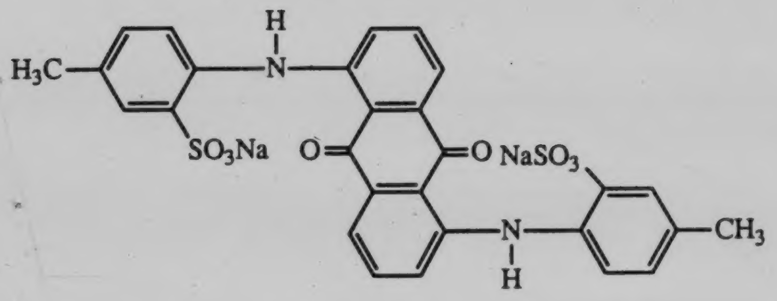
1. DPD


H_5C_2
N
C_2H_5
NH_2

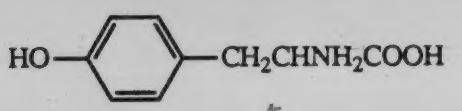
2. CHLOROPHENOL RED


OH
Cl
OH
Cl
O
S
O
O

3. ACVK


H
N
H_3C
SO_3Na
O
O
$NaSO_3$
N
H
CH_3

4. TYROSINE


HO
CH_2CHNH_2COOH

including manganese (III), chloramines and free halogens. Additional problems are that DPD reagent solutions are pH sensitive, and degrade with time. Despite the low detection limit, this method has too many problems and interferences to be considered useful.

2.4.5.2 Chlorophenol Red (CPR)

The chlorophenol red method, initially developed by Wheeler and co-workers[70] and later modified by Harp and Klein[71], is based on the fact that chlorophenol red (Figure 2.3) reacts specifically with chlorine dioxide while remaining essentially unresponsive to other chlorinated, and most other oxidizing compounds in solution. One mole of CPR reacts with two moles of ClO_2 to form a colorless product; the net decrease in absorbance at 575 nm is measured.

The three reagents required for this analysis are commercially available from the Hach Chemical Co (Loveland, CO), who have promoted the procedure and made it a relatively simple method to perform. These reagents are: reagent 1, a pH 5.2 citrate buffer solution; reagent 2, a 4.33×10^{-4} M CPR solution; and reagent 3, a pH 10 adjustment buffer.

The procedure can be slightly modified by changing the sample and reagent volumes to accomodate a range of concentrations of chlorine dioxide in the sample, but the overall sequence of events in the analysis is unchanged. As an example, the procedure for samples and standards in the concentration range 0 to 1.0 mg/L of chlorine dioxide is as follows:

To two 50-mL aliquots of sample (contained in stoppered flasks) 1.0 mL of reagent 1 (see above) is added to each aliquot and mixed. A small amount (0.06g) of sodium thiosulfate ($Na_2S_2O_3$) is added to one of the flasks to dechlorinate the solution and produce a blank. Exactly 1.0 mL of reagent 2 is added to both flasks and mixed well. Finally, 1.0 mL of reagent 3 is added to both flasks and again the solutions are mixed. The blank and sample absorbances are measured at 575 nm on a UV- visible spectrophotometer using 1-cm path length cells. The concentration is determined from a standard calibration curve. Note that in the calibration curves it is the change in absorbance (δA), corresponding to sample absorbance minus blank absorbance, that is plotted against chlorine dioxide concentration rather than the sample absorbance alone. The blank is used to compensate for minor variations in sample temperature.

A detection limit of 0.004 mg/L has been reported for this method[71] using a very long path length (25 cm) cell, but using a 1-cm cell the detection limit is of the order of 0.02 mg/L . The working range is up to 1 mg/L of chlorine dioxide. Some basic interference studies have been done on this method that seem to indicate good selectivity. Only free chlorine is said to interfere with the method, but the extent of interference has not been reported.

2.4.5.3 Acid Chrome Violet Potassium (ACVK)

This method, developed by Masschelein[72], was recently updated by the same author[73]. It has received little attention despite the fact that it appears to be very selective. ACVK (Figure 2.3) reacts selectively with chlorine dioxide, undergoing decolorization in the same way as CPR. The change in absorbance at 548 nm is monitored on a conventional spectrophotometer.

A stock solution (2×10^{-4} M) of indicator is prepared by dissolving 124.45 mg of ACVK in 200 mL of distilled water in a 1-L volumetric flask. To this is added 20 mg of sodium hexametaphosphate, 48.5 g of ammonium chloride, and 1.6 g of concentrated ammonium hydroxide. The last two reagents provide a buffer to ensure that the pH of the stock solution is in the range 8 to 10. The solution is diluted to one litre and stirred overnight prior to use.

In the analysis procedure 20-mL of the stock solution is placed in a 200-mL volumetric flask and diluted to volume with the sample water. The absorbance is measured in 4 or 5-cm cells at 548 nm and compared with that of a similar solution made up with blank water. A standard calibration curve is used to determine the concentration of chlorine dioxide in the sample.

A detection limit of 0.02 ± 0.01 mg/L[73] (using a 5-cm cell) has been reported for this method, with a working range of 0 to 25 mg/L. Initial studies of possible interference by several chlorinated species indicate that the method is quite selective. This method has been applied to the analysis of chlorine dioxide in wastewater[74] with some success and certainly warrants further study.

2.4.5.4 Tyrosine Oxidation

A method[75] has been developed based on the fact that chlorine dioxide oxidizes tyrosine (Figure 2.3) to dopaquinone. The absorption of dopaquinone can be measured spectrophotometrically at 490 or 355 nm.

The reagent solution is prepared by dissolving 750 mg of tyrosine in 8 mL of 1M sodium hydroxide and diluting to a volume of 125 mL with distilled water. Two acetate buffer solutions of pH 4.65 and pH 4.45 are also required.

To a 50-mL volumetric flask cooled in an ice bath is added 10-mL aliquots of sample and pH 4.65 buffer solution; the solution is then diluted to volume. In a separate 100-mL volumetric flask at room temperature a second solution containing 80 mL of distilled water, 6 mL of tyrosine reagent, and 2 mL of pH 4.45 buffer is prepared. A 10-mL aliquot of the buffered sample solution is added to the tyrosine solution and the solution diluted to volume with distilled water. The absorbance at 490 nm is measured and converted to concentration by means of a calibration curve.

The detection limit of this method is not very good (0.3 mg/L), and the working range was not given. No interference data on this method is available.

2.4.5.5 Other Colorimetric Methods

Although several other colorimetric methods have been developed for the analysis of chlorine dioxide, none have received much attention in recent years. They are briefly mentioned here for the sake of completeness.

Perhaps the best known of these additional colorimetric methods is the o-tolidine procedure developed by Aston[76], which uses oxalic acid and arsenite ion to suppress interferences and to slow down color development. The method is, however, reported to be pH sensitive and to have problems associated in obtaining reproducible results. A detection limit of 0.1 mg/L[62,76] has been reported. No data is provided on possible interferences. At one time this method appeared in Standard Methods[16], but it is no longer included.

Post and Moore[61] determined chlorine dioxide in surface water using 1-amino-8-naphthol-3,6-disulfonic acid (ANS), which develops an absorption peak at 525 nm in the presence of chlorine dioxide and hypochlorous acid. The latter is masked by the use of malonic acid. At the low pH (4.2) required in the method chlorite ion interferes.

Hoigne[77] has reported a method for the analysis of chlorine dioxide and ozone using potassium indigo blue trisulfonate. However, this method is carried out at pH 2 and therefore chlorite ion again will interfere. A detection limit of 0.01 mg/L has been reported for the method, but no interference data is available.

2.4.6 Chemiluminescence

Several papers have been published[78-80] using chemiluminescence as a basis for the analysis of chlorine dioxide. Chemiluminescent methods offer the advantages of having superior detection limits and selectivity over other methods, and in addition can be readily automated by use of, for example, flow injection analysis. The reagent commonly used in these systems is luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) either by itself or with hydrogen peroxide, which acts as a catalyst.

Saksa and Smart[78] reported a chemiluminescent method using a membrane flow cell constructed from a silicone polycarbonate copolymer. The reagent system used in this method was luminol and hydrogen peroxide. Detection limits for chlorine dioxide of 0.01 mg/L in natural waters and 0.02 mg/L in effluent waters were reported. Interference studies were reported for free chlorine only, although studies on the effect of other possible interferents are ongoing.

A system combining gas diffusion flow injection analysis and chemiluminescent detection has been reported[79]. In this method a specially designed spiral T- flow cell was directly mounted in front of a photomultiplier tube to maximize the detection of light from the chemiluminescent reaction. The reagent system used was luminol and hydrogen peroxide. A detection limit of 5 μg/L of chlorine dioxide was achieved, with a linear working range of 5 μg to 2 mg/L. Some interference testing was carried out for common species such as chloramines, chlorine, chlorite ion, and metal ions. No serious interferences were reported for this method.

From the above reports it would seem that these methods are quite promising. One major drawback, however, is that the instrumentation required for chemiluminescent methods is complex and relatively expensive.

2.4.7 Flow Injection Analysis (FIA)

Flow injection analysis techniques can be combined with other techniques in addition to chemiluminescence as detailed above.

A paper by Hollowell and co-workers[81] reported a sensitive method of analysis for chlorine dioxide which combined gas diffusion flow injection analysis and spectrophotometric detection. In this technique the analyte must first pass through a microporous membrane before it is detected. Because the membrane allows only gaseous species to pass through, a number of possible interferences are eliminated. The detection system is a conventional UV-visible spectrophotometer equipped with a 5- mm path-length flow cell. The absorbance at 359 nm, the characteristic wavelength of maximum absorption for chlorine dioxide, was monitored. The observed detection limit for chlorine dioxide was 0.25 mg/L with a linear working range of 0.25 to 142 mg/L. A small interference was observed for chlorine but other species which normally interfere, such as chlorite ion and metal ions, do not pass through the microporous membrane and therefore are not a factor.

A kinetic based flow injection/iodometric method for the determination of various chlorinated species, including chlorine dioxide, has been reported by Gordon and co-workers[82]. The detection system involves spectrophotometric monitoring of iodine produced by the reaction of the chlorinated species with potassium iodide at a wavelength of 370 nm. The detection limit for chlorine dioxide for this method is given as 0.3 mg/L, with a linear range of 0.3 to10 mg/L. Interferences in the method are reduced by "masking out" possible interferent species with specific reagents.

Methods involving flow injection techniques will continue to play a role in chlorine dioxide analysis. The many advantages that FIA systems offer, such as reproducible sample handling and timing, make them attractive, particularly if one requires the method to be automated. One additional advantage to this technique is the fact that much of the instrumentation required is simple and quite inexpensive.

2.4.8 Other Electrochemical Methods

Electrochemical techniques other than those involving amperometric titrations have also been developed for chlorine dioxide analysis. For example, a platinized microelectrode[83] with periodic renewal of the diffusion layer has been used to determine both chlorite ion and chlorine dioxide. The detection limit for chlorine dioxide is approximately 1.3 mg/L. No data on possible interferences was reported.

A multi-step procedure has been reported[84] for the determination of a number of chlorine and oxychlorine species. Chlorine dioxide is determined by glassy carbon electrode voltammetry. The detection limit reported for this method is poor (32 mg/L) and in addition free chlorine (HOCl and OCl^-) interferes.

Continuous electrochemical analyzers have also been developed[65]. In general these are designed to monitor chlorine or ozone. Typically they consist of flow-through amperometric cells with either copper or gold electrodes in contact with the solution. The advantages of these analyzers are that they are simple, have no moving parts, and need no special reagents. On the other hand they are subject to severe interferences from chlorine, and in some cases chloramines. Attempts to use these systems for the analysis of chlorine dioxide have not been particularly successful.

Membrane amperometric probes[85] have essentially the same advantages as the systems described above, and in addition can be placed directly in the process stream. The membrane protects the electrode from the environment, but more importantly provides additional selectivity. A membrane amperometric cell for chlorine dioxide was reported by Ogawa and Naito[85]. This consisted of a gold cathode held in contact with a gas permeable polymer film (Celgand 2400). The remote anode is pure silver. The electrolyte used was a mixture of 0.1 M potassium bromide and 0.1 M EDTA. The EDTA complexes the silver as it is oxidized and therefore keeps the surface clean. The probe responds to hypochlorous acid and chloramines at a level approximately one tenth of that for chlorine dioxide. Other halogens are reported to interfere with the method.

A rotating voltammetric membrane electrode was reported[86] using a silicone rubber/polycarbonate membrane. A detection limit of around 0.05 mg/L has been achieved for this method. No specific details on interferences are available but it is reported that chlorite ion, chlorate ion, hypochlorite, and several metal ions do not interfere. The effects of chlorine and chloramines are not discussed.

A voltammetric membrane electrode has been modified and applied to the analysis of chlorine dioxide[87]. The system consists of a gold cathode and counter electrode with a Ag/AgCl reference electrode. The system is placed behind a silicone rubber membrane. In the pulse mode a detection limit of 15 μg/L of chlorine dioxide was observed. Few interferences were reported for the method, the major one, hypochlorous acid, being minimized by masking with malonic acid. Other species such as chlorite ions and chlorate ions do not interfere.

2.4.9 Miscellaneous Methods

The only method of note not previously commented on is the use of electron spin resonance (ESR) techniques to determine chlorine dioxide[74,88]. Chlorine dioxide has an unpaired electron and therefore can be detected using this method. Detection limits of less than 1 mg/L have been reported. Interferences in the method were not discussed.

2.4.10 Summary

As can be seen from the above review there is certainly a need for improved methods for chlorine dioxide. An ideal method would be direct, suffer no inteferences, have a detection limit of 0.01 mg/L of chlorine dioxide or better, and be applicable to all water samples regardless of source. None of the methods described in this review satisfactorily fulfils all these criteria. At present the methods of choice appear to be either amperometry, colorimetry using a reagent, or UV-based direct spectrophotometry. The amperometric titration sequence devised by Aieta and co-workers[66] looks promising both for process control and for trace analysis. However, the interferences associated with this method need to be fully evaluated. A direct UV method appears to be satisfactory for the standardization of chlorine dioxide solutions, but seems unlikely to be applicable to the analysis of real samples owing to interference from UV absorbers.

Of the colorimetric reagent methods the two most promising appear to be the chlorophenol red (CPR) method developed by Wheeler[70] and the acid chrome violet potassium (ACVK) method developed by Masschelein[72,73]. The latter is particularly attractive in that there appear to be few interferences, and the pH range (8 to 8.5) of the method falls in the normal range over which water treatment is carried out. The chlorophenol red method appears to be sensitive but interference studies are incomplete.

Methods based on flow injection analysis (FIA) should also be investigated more thoroughly. The coupling of colorimetric or chemiluminescent methods to FIA may well produce more sensitive procedures.

The methods based on electrochemical techniques seem to have a way to go before they can be considered for routine analysis. The voltammetric membrane electrode developed by Dormond-Herrera and Mancy[87] looks promising and deserves further study. In general, however, these methods appear to suffer from serious interferences from other species in solution.

As a final note it would seem that more comparison studies are also required if the relative merits of both current and future methods for the analysis of chlorine dioxide are to be fully evaluated.

Experimental Work

2.5.1 Introduction

When solutions containing chlorine dioxide are prepared certain precautions are necessary to ensure accurate work. These include the need for high purity distilled water and chlorine dioxide demand-free glassware. The latter is desirable because a number of chemicals may adhere to the surface of the glass and either catalyze the decomposition of or react directly with chlorine dioxide. All glassware used in this work was "cured" by soaking in concentrated (300-400 mg/L) chlorine dioxide solution for 24 hours, and then rinsing thoroughly with distilled water. Distilled water only was used from then on to clean the glassware as required. High purity distilled water was obtained from a Milli-Q water purification system (Millipore Corp, Bedford, Mass). This water was boiled and stored in the refrigerator at 4° C until use. All amperometric titrations were carried out on a Fischer-Porter (Warminster, Pa) model 17T 2012 amperometric titrator coupled to a Metrohm Dosimat model 655 automatic burette (Metrohm Ltd, Herisau, Switzerland) which is capable of delivering a minimum volume of 0.001 mL. End points were detected by a special dual platinum-platinum combination electrode (also supplied by Fischer-Porter). All spectrophotometric measurements were made on a Shimadzu UV-160 recording spectrophotometer (Shimadzu Corp, Kyoto, Japan). All pH measurements were made on a Fisher Accumet 825 MP meter equipped with a Fisher pH glass electrode and calibrated with standard buffers (Fisher Scientific, Nepean, Ont) at two pH values (pH 4 and 8). All reagents and titrants were used without further purification unless otherwise indicated. Stock chlorine dioxide solutions were obtained either directly from the generator (plant #1) at the Rossdale water treatment plant or were prepared using the method outlined by

Masschelein[89]. Further details of the preparation of chlorine dioxide solutions will be found in the relevant section of this thesis.

2.5.2 Preliminary Work. Evaluation of Generator Produced Chlorine Dioxide by the Aieta Method

To evaluate the purity of the chlorine dioxide produced by the generating system (Rio Linda Chemical Co, Rio Linda, Cal) at the Rossdale treatment plant[90], several samples were collected and analyzed by the Aieta method[66] outlined in section 2.4. The procedure for the collection of samples was as follows:

[Note: Concentrated chlorine dioxide solutions are highly toxic. A respirator mask and disposable plastic gloves must be worn when a sample is being taken]. Chlorine dioxide is volatile and precautions should be taken to minimize contact of the sample with air. A sample was obtained by placing the flexible sample line of the generator into the bottom of the sample container (a dark Nalgene polyethylene bottle) and allowing several container volumes to overflow. After the bottle was filled the sample line was removed and the bottle tightly capped so that no headspace was present above the sample. Once this operation was completed the sample line valve was completely shut off.

Before sample analysis could be carried out it was necessary to standardize the 0.1 M sodium thiosulfate titrant (Fisher Scientific, Nepean Ont). A procedure outlined in Standard Methods[16] was used; it is outlined in the next section.

Standardization of 0.1 M Sodium Thiosulfate ($Na_2S_2O_3$)

In this procedure sodium thiosulfate ($Na_2S_2O_3$) is standardized with potassium iodate (KIO_3). To prepare a 0.01M solution, 1.070 g of potassium iodate (Anachemia, Toronto, Ont) was quantitatively transferred into a 500-mL volumetric flask and diluted to the mark with distilled water. Starch indicator was prepared as a thin paste by combining 1g of starch (BDH chemicals, Toronto, Ont) with 25 mL of distilled water. After mixing, a further 150 mL of distilled water was added and the mixture was boiled until a clear solution was obtained. The solution was removed from the heat and allowed to cool.

An aliquot (50-mL) of potassium iodate solution was pipetted into a 250-mL erlenmeyer flask. To this was added approximately 2 g of solid potassium iodide (Fisher Scientific, Nepean, Ont) and 10 mL of 1M hydrochloric acid. This solution was immediately titrated with thiosulfate (from a standard 50-mL buret) until the solution turned pale yellow. An aliquot (5-mL) of starch indicator was added; the solution immediately turns dark blue due to the formation of a starch-iodine complex. The solution was titrated further with thiosulfate to the first permanent disappearance of the blue color. Other aliquots of iodate solution were then treated in a similar manner to that described above to ensure reproducible data. The relevant equations are:

$$IO_3^- + 5\,I^- + 6\,H^+ = 3\,I_2 + 3\,H_2O \quad (1)$$

$$I_2 + 2\,S_2O_3^{2-} = 2\,I^- + S_4O_6^{2-} \quad (2)$$

From these two equations we can see that one mole of iodate requires six moles of thiosulfate for titration. Using this fact, the titration volumes, and the molarity of the iodate solution, the average concentration of the thiosulfate solution could be determined.

Procedure. The four steps involved in the Aieta procedure have been previously described in section 2.4 of this thesis. In determining the composition of the chlorine dioxide solutions produced from the generator a sample of between 5 and 10 mL was required. In the interests of clarity, and to highlight several important points, the overall experimental procedure will be briefly reviewed.

Step 1 (pH 7)

To a 250-mL beaker was added a quantity (190 to 200 mL) of distilled water and 2 mL of pH 7 phosphate buffer (Fisher Scientific, Nepean, Ont). An aliquot (5 to10 mL) of generator sample was then pipetted into the beaker, taking care to ensure that the tip of the pipet was well below the level of the water as the sample was delivered. A quantity (1g) of solid KI (Fisher Scientific, Nepean, Ont) was added and the solution titrated to an amperometric end point (see below) with sodium thiosulfate. The titrator is equipped with a stirrer to agitate the solution during the course of the titration. Once the KI has been added the solution must be immediately titrated to prevent the possibility of iodate formation[66].

Step 2 (pH 2)

To the solution from the previous step 2 to 3 mL of 6M hydrochloric acid was added, and the solution allowed to stand in the dark for five minutes. It may then be re-titrated with thiosulfate as before.

Step 3 (pH 7)

To a special gas washing bottle was added 190 to 200 mL of distilled water and 2 mL of phosphate buffer. A fresh aliquot of generator sample was pipetted into the bottle as described above and the solution was purged for 20 minutes with nitrogen which has been bubbled through a 5% KI scrub solution. The solution was transferred into a 250-mL beaker, 1g of KI was added and the solution immediately titrated with thiosulfate as before.

Step 4 (pH 2)

This last step is analogous to step 2, and is carried out on the purged sample from step 3 above.

Calculations.

The species which are determined in each of the four steps above can be summarized as follows;

Step 1 (A mL)	Cl_2 + 1/5 ClO_2
Step 2 (B mL)	4/5 ClO_2 + ClO_2^-
Step 3 (C mL)	Cl_2 not removed by N_2 purging
Step 4 (D mL)	ClO_2^- present in the original sample

From the titration volumes obtained for each of the steps (each step was performed in triplicate to ensure reproducible data) and the volume of sample aliquot used, the concentrations of the various species can be determined (in mg/L) from a series of equations. These equations are given in Table 2.1.

The amperometric titrations in this method are performed with a dual platinum-platinum electrode (Fischer-Porter) as stated above. The electrodes are immersed in solution and a small potential difference (around 0.1V) is applied between them. The electrode at a more positive potential acts as the anode, and any electroactive species present in solution will be oxidized at this electrode. Conversely the less positive electrode acts as the cathode and reduction of electroactive species will occur here. No current can flow between the electrodes unless a substance that can be oxidized and a substance that can be reduced with a potential difference of no more than 0.1 V are present in solution. In the Aieta method the electroactive species is iodine. When the solution contains both iodine and iodide, iodide will be oxidized to iodine at the anode while the converse process will occur at the cathode. The potential difference between these processes is zero.

Table 2.1

Equivalent Weights and Equations Needed to Calculate the Concentrations of Various Chlorine Species on the Basis of Mass in the Aieta Method.

(a) Equivalent Weights[62]

pH	Chlorine Species	Molecular Weight	Electrons Transferred	Equivalent Weight
		(mg/mol)		(mg/eq)
7	Chlorine Dioxide	67452	1	67452
2	Chlorine Dioxide	67452	5	13490
7, 2	Chlorine	70906	2	35453
2	Chlorite ion	67452	4	16863

Note

Equivalent Weight = Molecular Weight (mg/mol)/ Electrons transferred in the reaction.

(b) Equations To Determine Chlorine Species in the Aieta Method

(1) Chlorine (mg/L) = $[A - (B-D)/4] \times M \times 35453 / V_{sample}$.

(2) Chlorine Dioxide (mg/L) = $(5/4) \times (B-D) \times M \times 13490 / V_{sample}$.

(3) Chlorite ion (mg/L) = $D \times M \times 16863 / V_{sample}$.

In the above equations M is the molarity of the standardized sodium thiosulfate titrant, A, B, D are the titration volumes obtained in the various steps (mL), and V_{sample} is the aliquot of generator sample used (in mL).

The % yield of chlorine dioxide calculated from the generator sample is given by:

% yield = $[ClO_2] / [ClO_2] + [ClO_2^-]$

If a solution of iodine alone is titrated with a non electroactive reductant (such as sodium thiosulfate) then initially only iodine will be present in solution. No current will flow because no species that can be oxidized at the anode potential is present. However, as soon as a portion of iodine is reduced to iodide, then oxidation and reduction can both occur and a current will flow which can be detected on the milliammeter of the titrator. This current gradually decreases as the iodine is reduced and at the end point will be zero. Therefore at the end point of the titration no further change in the value of the current will be observed on the milliammeter.

Results. The composition of the chlorine dioxide samples, collected from the Rossdale generator (plant #1) over a period of several days and analyzed as described above, was as follows:

Chlorine = 200 ± 100 mg/L.

Chlorine dioxide = 1000 ± 200 mg/L.

Chlorite ion = 20 ± 10 mg/L

Yield = 95 to 100 % conversion of sodium chlorite to chlorine dioxide.

From these results, which were based on the average of eight analyses, we can see that the chlorine dioxide produced by the generator contains relatively little chlorite ion but a sizeable amount (around 20%) of chlorine. This is because the feed of sodium chlorite and chlorine in the Edmonton system is usually maintained so that there is a slight excess of chlorine present. The excess chlorine will be consumed by ammonia already added to the water (see Chapter 1) and will be converted into chloramines[17,18] to serve as secondary disinfectants in the distribution system. Excess chlorite ion present in the water will decompose over time, but a certain proportion remains in the water entering the distribution system. Concerns have been expressed over the potential health risks of chlorite[55,91]. Because the regulatory limit of total oxidants (primarily chlorite ion) imposed on the treatment plants is 0.5 mg/L, excess chlorite ion produced by the generation of chlorine dioxide could produce a sufficiently high concentration in the water to violate this condition. The concentration of total oxidants in the water is therefore monitored on a daily basis as stated in Chapter 1.

The amount of chlorine in the generator chlorine dioxide of the Edmonton system was considered too high to make reliable stock solutions of chlorine dioxide of an adequate purity for our purposes . Over time chlorine and chlorine dioxide react[54] to produce a number of species, including chlorate ion. In addition, chlorine is a major interference in a number of methods for the determination of chlorine dioxide (see review) and is itself a strong oxidant capable of undergoing reactions with a large number of inorganic and organic compounds. We therefore considered other methods to produce pure chlorine dioxide on a laboratory scale.

2.5.3 Preparation of Chlorine Dioxide by the Masschelein Procedure

Pure chlorine dioxide is often defined as a solution which contains chlorine dioxide as the only oxidative chlorine compound. It is extremely difficult to prepare in high purity. Although a number of methods have been described in the literature[16,89,92], many have a number of possible side reactions which lead to the formation of unwanted by-products such as chlorine. In 1967 Masschelein[89] reported that pure solutions of chlorine dioxide could be produced by the reaction of acetic anhydride with sodium chlorite ion in aqueous solution. No chlorine was produced and no further purification steps were required. This is particularly desirable because purification often requires that the chlorine dioxide be re-dissolved in water from the gas phase as the final step of the process. As mentioned previously, chlorine dioxide in the gas phase can be a major explosion hazard under certain circumstances[54] and so this procedure is not recommended. In view of this it was decided to try the Masschelein method and analyse the composition of the resultant chlorine dioxide by the Aieta titration method.

Procedure. A quantity (1g, 0.011 mol) of sodium chlorite (90.1%, Erco Industries, Tor, Ont) was dissolved in 900 mL of chilled distilled water contained in a dark glass bottle (1-L capacity). To this was added 2.25 g (0.022 mol) of reagent grade acetic anhydride (Caledon Laboratories, Georgetown, Ont) with constant stirring. The acetic anhydride was rapidly hydrolyzed and the reaction was complete within a matter of seconds. The bottle was stoppered and the chlorine dioxide solution stored in the refrigerator at 4°C until required. Fresh solutions of chlorine dioxide were prepared on a weekly basis.

The stoichiometry of this process has not been fully documented but one possible explanation involves the following two reactions.

$$(CH_3CO)_2O + H_2O = 2\,CH_3COOH \qquad (1)$$

$$2\,NaClO_2 + (CH_3CO)_2O + H_2O = ClO_2 + NaCl + CH_3COOH + H^+ + CH_3COONa + O_2 \qquad (2)$$

The acid produced may be neutralized by alkali present in the sodium chlorite or take part in one of several possible reactions of sodium chlorite with acids[93]. An increase in the acidity of the solution is observed during the process[89] and for experiments in distilled water the final pH is between 3.5 and 4.2.

The formation of oxygen during the reaction has been shown by polarography[89], however, chlorine dioxide interferes in this technique. In very concentrated solutions of sodium chlorite and acetic anhydride the following reaction may also occur:

$$4\,NaClO_2 + 2\,(CH_3CO)_2O + H_2O + 2\,ClO_2 = NaClO_3 + NaCl + 2\,CH_3COOH + 2\,CH_3COONa \qquad (3)$$

Results. Four batches of chlorine dioxide were prepared using a 2:1 molar ratio of acetic anhydride and sodium chlorite. By means of the Aieta titration procedure (triplicate analyses were performed) the following concentrations of chlorine dioxide, chlorite ion, and chlorine were obtained. These values are the averages obtained from the four batches of chlorine dioxide prepared. Uncertainties are ± 1 standard deviation.

Chlorine dioxide = 260 ± 30 mg/L

Chlorite ion = 25 ± 15 mg//L

Chlorine = 10 ± 5 mg/L

The source of the chlorite ion appears to be unreacted starting material. In the original paper it is claimed that no sodium chlorite remains unreacted, but it is not clear whether any analysis was carried out to check whether this was in fact the case. The small amount of chlorine found most likely arises from errors in calculating the individual species in the Aieta method. Chlorine is calculated by difference from several titrations steps (see Table 2.1) and it is possible that uncertainties can arise in the subtractions. It is unlikely that chlorine forms during the original reaction since no obvious reaction pathway is available. In addition, the UV spectrum of chlorine dioxide produced in the reaction did not show the presence of active chlorine species (HOCl or OCl^-). None of several papers by Masschelein[73,89,94] on this method of preparing chlorine dioxide have indicated that chlorine is produced in this reaction.

During subsequent experiments on this method it was discovered that if the sodium chlorite solution is allowed to stand overnight before the addition of acetic anhydride, the amount of unreacted chlorite ion remaining is somewhat reduced. To ensure optimum results the initial concentration of sodium chlorite should be low (0.5 to 1g) and the molar ratio of anhydride to sodium chlorite should be maintained around 2:1. Although the overall yield of the reaction (based on the amount of sodium chlorite) is relatively low (45-50 %), this procedure produces chlorine dioxide of sufficient quality to produce reliable standards. When stored in the refrigerator at 4°C in a dark bottle, solutions remain stable for periods of up to two weeks.

2.5.4 Analysis of Chlorine Dioxide by Ultraviolet Spectroscopy

The use of ultraviolet spectroscopy as a "referee" method for the analysis of chlorine dioxide has been well documented (see literature review). The advantages of the method are that it is fast, simple, and free from interferences from other chlorine species. This is illustrated in Table 2.2, which gives the absorbtion maxima and molar absorptivities of a number of common chlorine and oxychlorine species:

Table 2.2. Spectral Properties of Several Common Chlorine and Oxychlorine Species.

Species	λmax (nm)	Molar Absorbtivity (M^{-1} cm^{-1})	Reference
Chlorine Dioxide	360	1250	56, 95
Chlorite	260	148	56, 113
Hypochlorous Acid	235	100	96, 97
Hypochlorite Ion	290	350	96, 97
Monochloramine	245	416	98, 99
Dichloramine	297	265	98, 99

As can be seen from the table no other chlorine containing species has a absorbance maximum close enough to that of chlorine dioxide to cause a major interference. The characteristic UV/Visible spectrum of chlorine dioxide is shown in Figure 2.2.

Procedure. The absorbance of chlorine dioxide follows Beers Law over a range of concentration from 0 to 500 mg/L (ppm)[62]. The detection limit is set by the path length (b) of the measurement cell.

The spectrophotometer (Shimadzu 160) used in this work was preset to a wavelength of 360 nm. Distilled water, which had previously been filtered (under vacuum) through a 0.45 μm cellulose nitrate filter (Sartorius, Gottingen, Germany), was used to fill the sample and reference cells. The cells were placed in the sample holder, and the instrument zeroed by pressing the autozero function key. The sample cell was removed and rinsed several times with the chlorine dioxide sample to be measured before being filled and replaced in the cell holder, and the absorbance recorded. This process was repeated with fresh portions of sample until three replicate measurements of sample absorbance had been obtained. The absorbance readings were converted to concentration of chlorine dioxide using the relationship:

$$C = A/1250 \times 67450/b$$

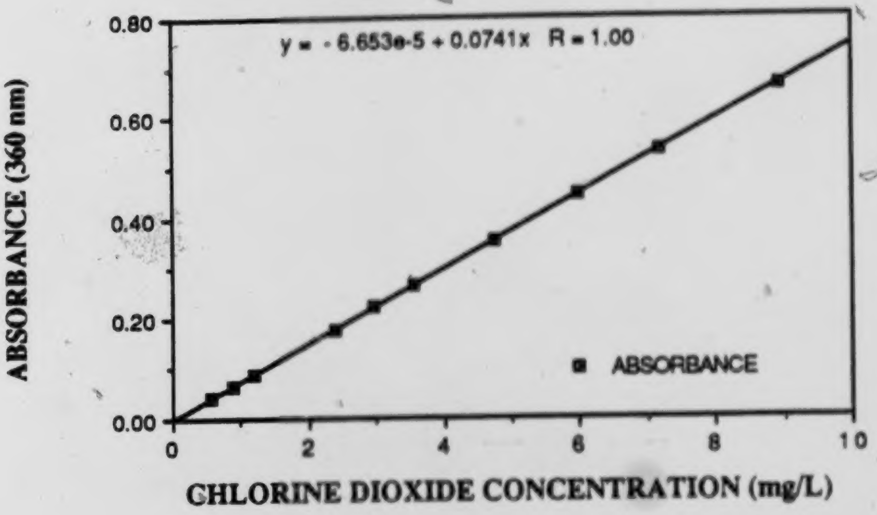
where C is the concentration of chlorine dioxide in the sample in mg/L (ppm), A is the average absorbance of the sample at 360 nm, 1250 is the molar absorbtivity of chlorine dioxide in M^{-1} cm^{-1}, 67450 is the molecular weight of chlorine dioxide in mg/mol, and b is the path length of the cell in cm.

In the special case where b=1 this term will not appear in the equation.

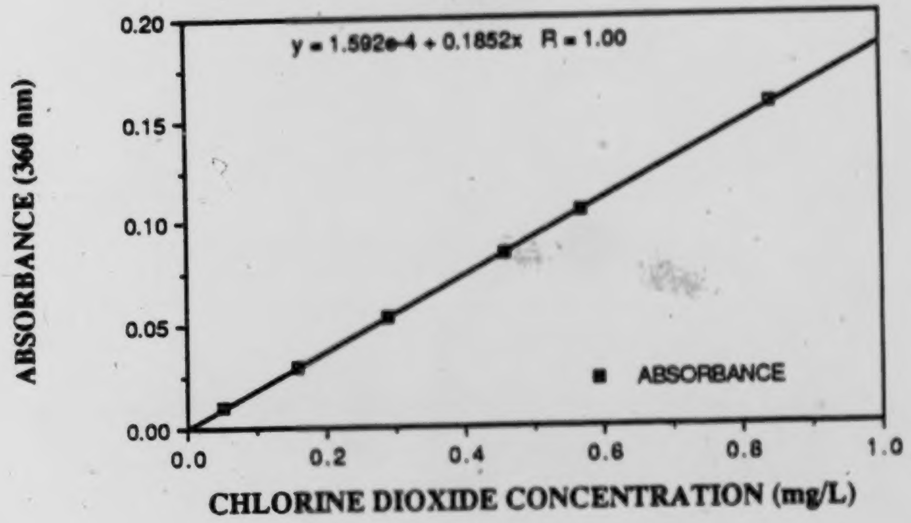
Results. Several calibration curves were plotted for dilute chlorine dioxide standards covering the concentration range from 0 to 50 mg/L (ppm) using cells of different path length. Two of these curves, from 0 to 10 mg/L (b = 4 cm), and from 0 to1 mg/L (b =10 cm), are shown in Figure 2.4. The limit of detection for the latter curve was 0.05 ± 0.02 mg/L, which is in accordance with values previously reported for this method[62,67].

Figure 2.4

(a) UV Calibration Curve for a Series of Chlorine Dioxide Standards From 0 to 10 mg/L Recorded on a Shimadzu 160 Spectrophotometer at 360 nm Using a 4-cm Path Length Cell.



(b) UV Calibration Curve for a Series of Chlorine Dioxide Standards From 0 to 1 mg/L Recorded on a Shimadzu 160 Spectrophotometer at 360 nm Using a 10-cm Path Length Cell.



2.5.5 Comparison of the Aieta and UV Methods

To determine whether the two methods previously described were equivalent a number of dilute chlorine dioxide standards were prepared and the chlorine dioxide concentrations obtained by the two methods compared.

Procedure. A number of standards in the range 0 to 50 mg/L were prepared by making the required dilution from a stock chlorine dioxide solution (prepared using the Masschelein procedure outlined earlier) into separate 250-mL volumetric flasks and filled to the mark with distilled water.

Triplicate analyses were obtained for both the Aieta and UV methods on identical freshly prepared solutions of each standard. The results of this initial study are summarized in Table 2.3 (a), which gives the average of three replicate analyses of chlorine dioxide for each of the standards by both methods. The final column is the percentage difference in the average value of chlorine dioxide found in the standards for each method. A discrepancy of between 10 and 20 % is present between the two methods. The values obtained by the Aieta method are consistently lower than those obtained by UV.

Several possible explanations may be considered to explain the lack of agreement. The Aieta method determines chlorine dioxide by difference (see Table 2.1). The total chlorite ion determined in step 4 is subtracted from the combined chlorite ion and chlorine dioxide determined in step 2 to give the overall concentration of chlorine dioxide. Clearly, an error in either of these steps will lead to an error in the value of the calculated chlorine dioxide concentration. A close look at the data collected in this work revealed that the ratio of chlorine dioxide to chlorite ion in the standards was not constant as would be expected. At higher concentrations of chlorine dioxide the ratio of chlorite ion to chlorine dioxide appeared to decrease, indicating that more chlorite ion

Table 2.3

Comparison of UV and Aieta Methods.

(a) Data Obtained From Initial Study

Std No.	Aieta Titration	Standard Deviation	Sample Volume	UV Method	Standard Deviation	% Diff
	(mg/L)	(mg/L)	(mL)	(mg/L)	(mg/L)	
# 1	4.01	0.05	20	5.07	0.11	20.90
# 2	6.25	0.24	20	7.01	0.11	10.84
# 3	9.78	0.23	20	11.54	0.16	15.25
# 4	11.60	0.13	20	13.38	0.16	13.30
# 5	13.71	0.21	20	15.38	0.11	10.86
# 6	18.57	0.26	20	22.01	0.22	15.62
# 7	20.15	0.12	20	24.44	0.22	17.55
# 8	22.60	0.48	20	27.24	0.16	17.03
# 9	25.59	0.47	20	30.43	0.11	15.91
# 10	34.19	0.32	20	40.03	0.27	14.59
# 11	36.05	0.57	20	42.46	0.16	15.10
# 12	42.39	0.64	20	49.66	0.27	14.64

(b) Data Obtained From Second Study

Std No.	Aieta Titration	Standard Deviation	Sample Volume	UV Method	Standard. Deviation	% Diff
	(mg/L)	(mg/L)	(mL)	(mg/L)	(mg/L)	
# 1	0.64	0.08	25	0.67	0.05	4.47
# 2	1.84	0.16	25	1.83	0.05	0.54
# 3	2.88	0.17	25	2.99	0.05	3.68
# 4	4.18	0.24	25	4.21	0.08	0.71
# 5	5.82	0.14	25	6.12	0.08	4.90
# 6	7.13	0.17	25	7.31	0.11	2.46
# 7	9.06	0.17	25	9.21	0.11	1.63
# 8	12.00	0.93	20	12.24	0.11	1.96
# 9	14.20	0.65	20	15.16	0.11	6.33
# 10	19.16	1.08	10	20.16	0.14	4.96
# 11	23.77	0.89	10	25.53	0.19	6.89
#12	27.26	0.42	10	28.19	0.22	3.30
#13	30.91	0.64	10	32.21	0.27	4.04
# 14	34.91	0.34	10	36.26	0.24	3.72

was forming. The calculated chlorine dioxide concentration will then be lower than expected, after the subtraction of the chlorite ion to give the final result. One explanation for this may be the conversion of a fraction of the chlorine dioxide to chlorite ion during the purging step (step 3) at pH 7. To minimize this problem it is necessary that the sample volume be kept to a minimum. This is especially important for higher concentrations of chlorine dioxide in the standards.

The purging time of the solution must also be optimized. Sufficient time has to be allowed for the chlorine dioxide to be stripped from solution, but not so long as to allow conversion of chlorine dioxide to chlorite ion to any great extent. Purging should also be carried out at a moderate rate because too high a rate can cause loss of sample, and may accelerate the conversion of chlorine dioxide to chlorite ion.

Several other potential sources of error in the method should be considered. One is the use of 6M hydrochloric acid in steps 2 and 4. In strongly acidic solutions the oxidation of iodide to iodine by dissolved oxygen can take place; this will affect titration values obtained in both steps 2 and 4. To minimize this the molarity of the acid was lowered to 2M, although the same amount as before (2 to 3 mL) was added to the solution. Better mixing of the acid and sample can also achieved by adding the acid from a standard 5-mL glass syringe while the solution is being stirred after completion of the first step.

Contamination of the sample can also occur from several sources. Between titrations the electrodes should be thoroughly rinsed with distilled water to remove traces of potassium iodide. Beakers and gas wash bottles should be rinsed between samples with distilled water to remove traces of former contents. The distilled water should be checked for the presence of active chlorine compounds by running 200-mL portions as blanks before any samples are analyzed.

After a thorough investigation of all aspects of the Aieta method, a second comparison study was carried which was identical to the first. The only minor difference was the fact that all UV measurements were recorded using a 2-cm path length cell for the second study in place of the 1-cm path length cell used in the initial study. All the precautions mentioned above for the Aieta method were strictly adhered to. The results obtained from this second study are shown in Table 2.3 (b).

As can be seen from the data much better agreement between the two methods was obtained in the second study. The percentage differences in the average values by the two methods were considerably less than obtained previously. The agreement between the two methods was particularly good at low concentrations of chlorine dioxide. This was encouraging since it was our intention to go to lower levels in the next stage of the project.

As a result of this work several observations concerning the Aieta and UV methods can be made. The Aieta method originally developed for the analysis of generator samples of chlorine dioxide had not been directly compared with other methods prior to this study. As is shown from this work the results obtained with this method are comparable to those obtained by the UV method providing the precautions outlined are followed. The procedure that must be followed in the Aieta method is not simple and requires considerable experience for satisfactory results. It is slow, requiring of the order of 40 to 50 minutes to process one sample in triplicate through the four steps. Great care must be taken to ensure cleanliness in the experiment if reproducible results are to be obtained.

On the other hand, few problems were encountered with the UV method. It is a fast, direct, and simple. Data obtained with this method were very reproducible, and for determining the concentration of chlorine dioxide in standards it is an excellent method.

The problems encountered with the Aieta method are somewhat indicative of the weaknesses of methods which involve the determination of species by difference. Direct methods are preferred whenever possible. However, our results clearly indicate that the Aieta method can be a useful "referee" method for chlorine dioxide analysis.

2.5.6 The Chlorophenol Red (CPR) Method

As stated in the review section, the chlorophenol red method[70,71] appears to be a sensitive colorimetric procedure for the determination of chlorine dioxide. The three reagents required (see review) are commercially available from the Hach Chemical Company (Loveland, CO). In this work standard calibration curves covering the ranges 0 to 1 and 0 to 0.15 mg/L were prepared. Dilute solutions of chlorine dioxide were standardized using both the Aieta and UV methods described earlier. The absorbance of the samples was measured at 575 nm on either a Shimadzu 160 or a Hach 2000 DR spectrophotometer. The latter is a portable instrument, designed primarily for field operation, that.contains a number of built-in programs, including one for chlorophenol red. The procedure for the construction of the calibration curves was as follows.

(a) Preparation of a 0 to 1.0 mg/L Calibration Curve

Procedure. Into each of two ground glass stoppered 50-mL graduated mixing cylinders was pipetted a 50-mL aliquot of sample solution. Exactly 1.0-mL of reagent 1 (a pH 5.5 buffer) was added to each cylinder and the cylinders were inverted several times to mix. Sodium thiosulfate (60 mg) was added to one of the cylinders and the contents mixed until the salt dissolved completely. This solution is the blank. Exactly 1.0-mL of reagent 2 (a 4.33×10^{-4} M chlorophenol red solution) was added to each cylinder and thoroughly mixed by inversion. Finally, 1.0-mL of reagent 3 (a pH 10 adjustment buffer) was added. The quantity of reagents added (particularly reagent 2) is important, and it is strongly recommended by the author that three labelled 1-mL pipettes (one for each reagent) be used for this purpose. To obtain optimum results the absorbance of the solutions should be measured as quickly as possible after the addition of the last reagent.

To measure the absorbance of the samples on the Shimadzu 160 spectrophotometer the same procedure outlined previously for the UV method was followed. The absorbance of the blank and the sample solutions were measured at 575 nm, using a 1-cm path length cell after the instrument had been zeroed with distilled water.

To measure the absorbance using the Hach DR 2000 portable spectrophotometer the procedure was as follows;

The stored program for the chlorophenol red method (#72) was recalled from the memory, and the wavelength dial rotated until the display read 575 nm. The Read/Enter button on the front panel of the instrument was pressed; "mg/L ClO_2 L" appears on the screen. A 25-mL aliquot of the blank solution was then pipetted into a special 2.5-cm path length cell supplied with the instrument and placed in the sample holder (only one cell can be placed in the holder at one time). After closing the light shield, the "zero" key on the instrument was pressed. After a few seconds the display shows "0.00 mg/L ClO_2 L", after which the cell was removed. A second matched cell containing 25 mL of the sample solution was then placed in the sample holder as before and the Read/Enter key pressed. The concentration of the sample (in mg/L) was recorded manually from the screen. A second sample reading was then taken by repeating the above procedure.

The chlorine dioxide concentrations obtained by the chlorophenol red procedure, when compared to those obtained by the UV and Aieta methods, were found to agree closely. For subsequent work samples were often measured on the Hach instrument by the chlorophenol red method as a check procedure. Another convenience of the Hach 2000 DR is that programs for other methods can be stored in the memory and recalled as required. This is potentially very useful.

(b) Preparation of a 0 to 0.15 mg/L Calibration Curve

Several minor changes to the method outlined in (a) above were required for this calibration curve.

Procedure. The required amount of sample was added to a 200-mL volumetric flasks and made up to the mark with distilled water. The reagents were added in the same order as before, but the quantities of each reagent added were: reagent 1 = 2 mL, reagent 2 = 0.5 mL, and reagent 3 = 2 mL. Sodium thiosulfate was added as before to one of the samples after the addition of reagent 1 to act as a blank. Sample absorbances were measured as previously described, except that a 10-cm path length cell was used to measure absorbances with the Shimadzu instrument.

The standard calibration curves prepared for this method are plots of the change in absorbance against concentration, where change in absorbance is defined as the absorbance of the sample minus that of the blank. The blank compensates for variations in temperature which may occur during the course of the experiment inasmuch as the color intensity of CPR is temperature dependant[71]. Since the reaction involves decolorization of a dye, the slopes of the plots are negative rather than positive.

Results. A set of data for these calibration curves is shown in Table 2.4. The results show the typical range of absorbance (and change in absorbance) obtained for a

Table 2.4

Chlorophenol Red (CPR) Calibration Curve Data.

(a) 0 to 1.0 mg/L

Aieta Titration Method	UV Method	Sample Abs (575 nm)	Blank Abs (575 nm)	Change in Abs (575 nm)
(mg/L)	(mg/L)			
0.03 ± 0.01	0.04 ± 0.02	0.695 ± 0.005	0.708 ± 0.002	0.013 ± 0.006
0.13 ± 0.02	0.13 ± 0.02	0.644 ± 0.005	0.701 ± 0.003	0.057 ± 0.006
0.21 ± 0.01	0.23 ± 0.01	0.603 ± 0.003	0.703 ± 0.004	0.100 ± 0.005
0.34 ± 0.02	0.34 ± 0.02	0.567 ± 0.006	0.713 ± 0.004	0.146 ± 0.007
0.44 ± 0.03	0.47 ± 0.01	0.500 ± 0.002	0.702 ± 0.002	0.202 ± 0.003
0.56 ± 0.02	0.59 ± 0.01	0.446 ± 0.004	0.704 ± 0.003	0.258 ± 0.005
0.68 ± 0.02	0.70 ± 0.02	0.416 ± 0.006	0.710 ± 0.003	0.294 ± 0.007
0.88 ± 0.03	0.92 ± 0.02	0.326 ± 0.003	0.710 ± 0.003	0.384 ± 0.004
0.98 ± 0.03	0.97 ± 0.02	0.297 ± 0.004	0.707 ± 0.002	0.410 ± 0.004

(b) 0 to 0.15 mg/L

Aieta Titration Method	UV Method	Sample Abs (575 nm)	Blank Abs (575 nm)	Change in Abs (575 nm)
(mg/L)	(mg/L)			
0.014 ± 0.01	ND	0.996 ± 0.005	1.050 ± 0.005	0.054 ± 0.006
0.030 ± 0.01	0.04 ± 0.02	0.924 ± 0.005	1.037 ± 0.006	0.113 ± 0.007
0.058 ± 0.01	0.07 ± 0.01	0.794 ± 0.004	1.049 ± 0.003	0.255 ± 0.005
0 083 ± 0.01	0.09 ± 0.02	0.649 ± 0.005	1.042 ± 0.005	0.393 ± 0.007
0.118 ± 0.01	0.12 ± 0.01	0.536 ± 0.005	1.038 ± 0.004	0.502 ± 0.006
0.146 ± 0.01	0.14 ± 0.01	0.446 ± 0.004	1.051 ± 0.006	0.605 ± 0.007

series of chlorine dioxide standards on the Shimadzu 160 spectrophotometer at a wavelength of 575 nm.. The average concentration of each standard was determined in triplicate by both the Aieta and UV methods.

For the CPR procedure two replicate samples and one blank were prepared for each point on the curve. The absorbances of all the solutions were then measured in duplicate. For the samples the four readings obtained were then combined to give an overall average absorbance. A similar procedure was carried out to determine the average absorbance of the blank. This was then subtracted from the average sample absorbance to give the difference in absorbance plotted for the calibration curve. Since chlorophenol red is "bleached" when it reacts with chlorine dioxide the observed difference in absorbance increases with increasing concentrations of chlorine dioxide. The overall standard deviation associated with the change in absorbance was calculated from the equation:

$$\text{SD (overall)} = [(\text{SD blank})^2 + (\text{SD sample})^2]^{0.5}$$

where SD blank is the standard deviation associated with the average absorbance of the blank, and SD sample is the standard deviation associated with the average absorbance of the sample.

2.5.7 The ACVK (Masschelein) Method

This method, for which an updated procedure has recently been reported[73], has received little attention, despite the fact that initial interference studies would appear to suggest it is very selective. As with chlorophenol red, the decolorization of acid chrome violet potassium (ACVK) on reaction with chlorine dioxide forms the basis of the method. Two advantages reported for this method are that the procedure is straightforward and can be carried out at the normal pH range (7.5 to 9) of treated water.

Two calibration curves were constructed to cover the ranges 0 to 1.2 mg/L, and 0 to 0.15 mg/L of chlorine dioxide.

A stock solution (2 x 10^{-4} M) of ACVK indicator (Aldrich Chemical Co, Milwaukee, Wis) was prepared as described earlier in the literature review section of this thesis. ACVK is also known as Alizarin Violet 3R (CI 61710) and appears in a number of chemical supply catalogues under that name.

(a) Preparation of a 0 to 1.2 mg/L Calibration Curve

Procedure. Two 100-mL ground glass stoppered graduated mixing cylinders were used in this procedure. Into one cylinder was pipetted 100 mL of sample solution while into the other was pipetted 100 mL of distilled water to serve as a blank. Aliquots (5 mL) of buffered ACVK reagent were then pipetted into each cylinder and the contents mixed by inverting the cylinders several times. The solutions were then left for 2 to 3 minutes to allow the reaction to go to completion. The absorbances of the solutions were then measured in triplicate at 548 nm on the Shimadzu spectrophotometer using a 4-cm path length cell.

(b) Preparation of a 0 to 0.15 mg/L Calibration Curve

Procedure. Sample and blank solutions were prepared in separate 250-mL volumetric flasks. To each flask were added 10-mL aliquots of buffered reagent, and the solutions mixed. After 2 to 3 minutes the absorbances of the solutions were measured at 548 nm as before, using a 10-cm path length cell.

Results. A typical set of data obtained for these curves is shown in Table 2.5. The results give the typical range of absorbance (and change in absorbance) values obtained for a series of chlorine dioxide standards on the Shimadzu 160 spectrophotometer at a wavelength of 548 nm. As described earlier, the average concentration of each standard was also determined in triplicate using the Aieta and UV methods. Average

Table 2.5

Acid Chrome Violet Potassium (ACVK) Calibration Curve Data.

(a) 0 to 1.2 mg/L

Aieta Titration Method (mg/L)	UV Method (mg/L)	Sample Abs (548 nm)	Blank Abs (548 nm)	Change in Abs (548 nm)
0.13 ± 0.03	0.12 ± 0.02	0.225 ± 0.004	0.248 ± 0.002	0.023 ± 0.005
0.21 ± 0.02	0.22 ± 0.02	0.204 ± 0.001	0.249 ± 0.003	0.045 ± 0.003
0.34 ± 0.02	0.35 ± 0.01	0.192 ± 0.004	0.249 ± 0.002	0.057 ± 0.005
0.44 ± 0.04	0.43 ± 0.02	0.172 ± 0.002	0.249 ± 0.002	0.077 ± 0.003
0.53 ± 0.03	0.56 ± 0.01	0.151 ± 0.003	0.250 ± 0.002	0.099 ± 0.004
0.63 ± 0.03	0.65 ± 0.02	0.136 ± 0.002	0.248 ± 0.002	0.112 ± 0.003
0.88 ± 0.03	0.85 ± 0.02	0.103 ± 0.003	0.249 ± 0.003	0.146 ± 0.004
1.10 ± 0.04	1.12 ± 0.02	0.067 ± 0.003	0.250 ± 0.003	0.183 ± 0.004

(b) 0 to 0.15 mg/L

Aieta Titration Method (mg/L)	UV Method (mg/L)	Sample Abs (548 nm)	Blank Abs (548 nm)	Change in Abs (548 nm)
0.030 ± 0.01	0.04 ± 0.02	0.523 ± 0.003	0.537 ± 0.002	0.014 ± 0.004
0.055 ± 0.01	0.06 ± 0.01	0.514 ± 0.002	0.537 ± 0.003	0.023 ± 0.004
0 092 ± 0.02	0.10 ± 0.02	0.497 ± 0.003	0.538 ± 0.001	0.041 ± 0.003
0.125 ± 0.01	0.13 ± 0.01	0.490 ± 0.003	0.540 ± 0.002	0.050 ± 0.004
0.148 ± 0.01	0.15 ± 0.01	0.472 ± 0.002	0.537 ± 0.002	0.065 ± 0.003

absorbances and standard deviations were obtained in the same way as described for the chlorophenol red method in the previous section.

2.5.8 Interference Testing on Existing Methods

2.5.8.1 Introduction

The next stage of the project was to test the various methods for possible interferences by a number of common species present in treated water. This was necessary in part because quantitative interference data on the Aieta and chlorophenol red methods are incomplete. A list of the species tested in this study, the concentration of potential interferent used, and typical levels[100,101] found in City of Edmonton drinking water are shown in Table 2.6 below.

Table 2.6

Levels of Tested Interferent Species Found in the City of Edmonton Drinking Water.

Tested Species	Amount Added	Normal Levels in Drinking Water
	(mg/L)	(mg/L)
Chloride ion (Cl^-)	6.2	2.5 to 3.5
Chlorite ion (ClO_2^-)	1.5 to 6.9	0.2 to 0.5
Chlorate ion (ClO_3^-)	3.9	0 to 0.2
Hypochlorous Acid ($HOCl$)	2.0	Nil
Hypochlorite Ion (OCl^-)	2.0	Nil
Aluminium	1.05	0.1 to 1
Iron	0.6	0.001 to 0.020
Monochloramine (NH_2Cl)	2.0	1.8 to 2.2
Dichloramine ($NHCl_2$)	2.0	Unknown
Calcium	100	50 to 70
Copper	0.2	0.001 to 0.010

The value quoted above for monochloramine is that determined for the analysis of "total chloramines". At the normal pH range encountered for drinking water samples (8 to 8.5) monochloramine is assumed to be the only chloramine species present[17]. As a result no independent analysis for dichloramine is performed by the City of Edmonton laboratory.

Procedure. For each of the four methods the same test procedure was followed for all species tested. Each species was tested in standard solutions containing 0.1 ± 0.05 and 0.6 ± 0.05 mg/L of chlorine dioxide. Full details of the preparation and standardization procedures are given for each species studied. The results obtained are discussed in detail at the end of this section. The procedures were as follows:

(1) UV Method

Chlorine dioxide standards of the required concentration (0.1 or 0.6 mg/L) were prepared by dilution in separate 1-L volumetric flasks. For each test one chlorine dioxide standard was prepared and its absorbance determined in triplicate at 360 nm with a 10-cm path length cell as described earlier. A second solution containing chlorine dioxide and the species under test was prepared and the absorbance determined as before. Absorbances were converted to concentrations and the effect of the interferent species was determined by comparing the relative concentrations measured for the standards. As a check of the results obtained this procedure was repeated using a second set of freshly prepared solutions.

(2) Aieta Method

When determining chlorine dioxide concentrations below 1 mg/L the molarity of the sodium thiosulfate titrant must be reduced to 0.01M. The standardization procedure for the thiosulfate solution was as given earlier in this chapter.

Analysis of the dilute standards with and without the species under test was carried out in triplicate and the average chlorine dioxide concentration calculated and compared. The test species must be added prior to steps 1 and 3 in the analysis.

(3) Chlorophenol Red Method

The procedures followed for the 0.6 and 0.1 mg/L standards are described in sections 2.5.6 (a) and (b) respectively.

A set of three samples and one blank (containing sodium thiosulfate) was made up and the absorbance of all the solutions was measured in triplicate. A second set of solutions containing chlorine dioxide and the interferent species was prepared, and the absorbance of these solutions was measured in triplicate as before. For each set of solutions the average absorbance of each of the three samples and the blank solution was then determined. The average absorbance of the samples was subtracted from the blank to give the overall change in absorbance. The change in absorbance values was converted to concentration via a standard calibration curve.

(4) ACVK Method

The relevant procedures followed for the 0.6 and 0.1 mg/L standards are described in sections 2.5.7 (a) and (b) respectively. The experimental procedure for the testing was identical to that described above for the CPR method.

Interference Testing of Individual Species

2.5.8.2 Chloride Ion

Preparation of stock solution. A stock solution of approximately 620 mg/L of chloride was prepared by weighing (to the nearest 0.1 mg) 1g of sodium chloride (BDH chemicals, Toronto, Ont) into a 1-L volumetric flask and diluting to volume with distilled water.

Standardization. The chloride stock solution was standardized using Fajans method[102], a precipitation titration using an adsorption indicator. Here dichlorofluorescein (a weak organic acid) is used to determine the end point of the titration of chloride by silver ions. Since the indicator is a weak acid, at too low pH values only a small amount is present as the anion. An acetate buffer (pH 4.8) is normally added to control the pH during the titration.

A 0.014 M solution of silver nitrate, $AgNO_3$, was prepared by weighing 2.3945 g of $AgNO_3$ (Dixon Fine Chemicals, Sherwood Park, Alta) into a 50-mL beaker and transferring quantitatively into a 1-L volumetric flask. The flask was then filled to the mark with distilled water, mixed, and stored away from the sunlight until required to minimize photodecomposition.

A 0.015 M solution of standard sodium chloride was prepared by weighing (to the nearest 0.1 mg) 0.4116g of NaCl into a 50-mL beaker and transferring to a 500-mL volumetric flask. The flask was then filled to the mark with distilled water, mixed, and stored in the refrigerator until required.

Titration procedure[103]. Several aliquots of the standard (30 mL), and the stock chloride sample solution prepared earlier (25 mL) were pipetted into 250-mL erlenmayer flasks. An aliquot (10 ml) of distilled water was added to each. Before titrating, 1 mL of 0.5 M acetic acid-0.5 M sodium acetate buffer solution (pH 4.8) and approximately 0.1 g of dextrin was also added to each flask. For the first aliquot 5 drops of 0.1% dichlorofluorescein indicator was added and the solution titrated with silver nitrate until the precipitate turned pale pink. All subsequent aliquots were titrated with $AgNO_3$ to within 1 to 2 mL of the end point, indicator was then added and the titration completed with constant swirling of the solution. The equation for the reaction is:

$$AgNO_3 + NaCl = AgCl + NaNO_3$$

Since one mole of silver nitrate reacts with one mole of sodium chloride the molarity (M $AgNO_3$) of the silver nitrate titrant solution is calculated from the equation:

$$M\ AgNO_3 = M\ NaCl \times V\ NaCl / mL\ AgNO_3$$

where M NaCl = the molarity of the sodium chloride standard solution, V NaCl = the volume of the aliquot of sodium chloride used in the titration (30 mL), and mL $AgNO_3$ = the volume of silver nitrate titrant required to reach the end point. Once the molarity of the silver nitrate has been determined the concentration of chloride in the stock solution (in mg/L) can be obtained from the equation:

$$Cl^-\ Stock\ (mg/L) = mL\ AgNO_3 \times M\ AgNO_3 \times 35450 / V\ NaCl$$

where mL $AgNO_3$ is the volume of silver nitrate required to reach the end point, V NaCl is the volume of the aliquot of sodium chloride stock solution taken for the titration (25 mL), and 35450 is the molecular weight of the chloride ion in mg.

The chloride ion concentration of the stock solution was 621 ± 3 mg/L (based on four replicate analyses). Interference tests were then carried out at an added chloride concentration of 6.2 ± 0.3 mg/L for all methods. The results of these tests can be found in the tables at the end of this section.

2.5.8.3 Chlorite Ion

Preparation of stock solution. An approximately 600 mg/L stock solution was prepared by dissolving 1.002 g of sodium chlorite (90.1% pure, Erco Industries Ltd, Toronto, Ont) in a aliquot of distilledwater contained in a 1-L volumetric flask, and diluting to volume.

Standardization. The stock solution was analyzed by the last step (step D) of the Aieta amperometric procedure, which is designed to determine the total chlorite ion present in the sample. Since neither chlorine dioxide nor chlorine are present, the titration steps normally done to determine the concentrations of these species are not required.

Several 5-mL aliquots of the stock solution were pipetted into 250-mL beakers containing 190 to 200 mL of distilled water and 1g of potassium iodide (KI) added. A 3 mL aliquot of 2M HCl was then added with stirring to each solution with a syringe and the solutions placed in the dark for 5 minutes to react. The solutions were then titrated to an amperometric end point with 0.1M sodium thiosulfate. The concentration of chlorite ion in the stock solution was calculated using the equation already given in the discussion of the Aieta titration method. .

The stock solution contained 601 ± 3 mg/L of chlorite ion (based on three replicate analyses). Interference tests were carried out with varying amounts of added chlorite ion. The amount of chlorite ion added, and the results of the tests, are given at the end of this section.

2.5.8.4 Chlorate Ion

Preparation of stock solution. A stock chlorate solution was prepared by dissolving 1.006 g of sodium chlorate (J.T Baker Chemical Co, Phillipsburg, N.J) in a aliquot of distilled water in a 1-L volumetric flask, and diluting to volume.

Standardization. The method used for the analysis of chlorate is essentially an extension to the Aieta method. Because of the extremely acidic conditions which are required, bromide is used as the reducing agent for chlorate instead of iodide. This change is made because bromide is not oxidized to any great extent by dissolved oxygen under strongly acidic conditions, whereas iodide is.

Into a 125-mL ground glass stoppered erlenmeyer flasks was added 1-mL of freshly prepared 5% potassium bromide, and 10 mL of 12M hydrochloric acid. A 10-mL aliquot of 100-fold diluted chlorate stock solution was then carefully added to the flask, and the solution stoppered, mixed, and placed in the dark for 30 minutes to allow the reaction to go to completion. Solid potassium iodide (1g) was then added to the reaction mixture. The iodide is rapidly oxidized to iodine by the bromine formed as a result of the reaction between chlorate and bromide. The solution was then quantitatively transferred to a 250-mL beaker containing 25-mL of saturated disodium hydrogen phosphate (Na_2HPO_4, Mallinckrodt Inc, Paris, Ken) by thorough rinsing with distilled water and titrated to an amperometric end point with standard sodium thiosulfate.

The procedure was repeated using distilled water in place of the diluted chlorate stock solution to determine the blank value. Triplicate analyses were done for both the sample and blank determinations.

The concentration of chlorate (in mg/L) in the stock solution was determined from the equation:

$$ClO_3^- \text{ (mg/L)} = E \times M \text{ titrant} \times 13908 / V \text{ sample}$$

where E is the titration volume required for the sample minus that of the blank, M titrant is the molarity of the thiosulfate titrant, V sample is the size of the aliquot of dilute chlorate stock solution used , and 13908 is the equivalent weight of chlorate in mg/eq.

Interference tests were carried out at an added chlorate concentration of 3.9 ± 0.3 mg/L. It is strongly recommended that the above method only be used for solutions containing less than 10 mg/L of chlorate because the strongly acidic reaction conditions were found to be highly detrimental to the sensitivity of the platinum electrode at high chlorate concentrations. After completion of the titrations the electrode should be thoroughly rinsed with distilled water to remove all traces of the solution components.

2.5.8.5 Hypochlorous Acid

Chlorine gas rapidly hydrolyzes in aqueous solution, with equilibrium being attained in a matter of seconds[62]. The relevant equations are:

$$Cl_2\,(g) + H_2O = HOCl + H^+\ Cl^- \quad (1)\ \text{and}$$

$$HOCl + H_2O = H_3O^+ + OCl^- \quad (2)$$

The two chemical species formed by chlorine in water, hypochlorous acid (HOCl) and hypochlorite ion (OCl^-), are usually referred to as "free chlorine" species. The reactions shown above are reversible. The ratio of these two species in solution is highly dependent on solution pH, and to a lesser extent on solution temperature. At a pH of 4 or less hypochlorous acid is essentially the only species present in solution[62], whereas at pH 10 and above only hypochlorite ion is present. At intermediate pH values, both species are present to some extent. Hence by carefully controlling the pH, either of these species can be prepared in aqueous solution .

Preparation of stock solution. A hypochlorous acid stock solution (of approximately 200 mg/L) was prepared by pipetting a 50-mL aliquot of chlorine water (Anachemia, Montreal, Que) into a 1-L volumetric flask containing 300 to 400 mL of distilled water and 10 mL of 1M hydrochloric acid. The flask was filled to the mark and the solution was stored in a refrigerator until required. The absorbance of a portion of the solution was recorded in the UV region of the spectrum between 200 and 300 nm. Hypochlorous acid has a characteristic UV spectrum with an absorbance maximum at 235 nm ($\varepsilon = 100\ M^{-1}\ cm^{-1}$)[97].

Standardization. Hypochlorous acid stock solutions were standardized using step A of the Aieta amperometric titration procedure (see earlier section on the Aieta method). The concentration of the stock solutions were found to be in the range 164 ± 10 mg/L (as chlorine). Triplicate analyses were carried out for each determination. A fresh solution was prepared and standardized every two days because the stock solutions degrade with time. Interference tests were carried out at a hypochlorous acid concentration of 2 ± 0.1 mg/L. Details of these tests can be found at the end of this section.

2.5.8.6 Hypochlorite

Preparation and standardization of hypochlorite stock solution

A hypochlorite stock solution was prepared in a manner similar to that described for hypochlorous acid above, the only difference being that 10 mL of 1M sodium hydroxide was added in place of 1M hydrochloric acid to ensure that the pH of the solution was above 10. The UV spectrum of the solution was monitored as before. Hypochlorite also has an absorbance maximum in the UV region which occurs at 290 nm ($\varepsilon = 350\ M^{-1}\ cm^{-1}$)[97].

The method of standardization was analogous to that described earlier for hypochlorous acid. Stock solutions were analyzed in triplicate and were found to be in the range of 172 ± 10 mg/L as chlorine, based on triplicate analyses. Interference tests were carried out at the same levels as for hypochlorous acid.

2.5.8.7 Aluminium

Preparation and standardization of aluminium stock solution

Aluminium was the first of the metal species tested for possible interference effects in this study. A stock solution of approximately 100 mg/L, which also contained 3% by volume of concentrated nitric acid, was prepared from a certified aluminium standard (BDH Chemicals, Toronto, Ont). The stock solution was standardized, after dilution, by graphite furnace atomic absorption spectrometry (GFAAS). The method used was identical to that described for the metals analysis in chapter 1. The Varian

SpectrAA 300-400 AA instrument parameters and the conditions used in the analysis can be found in appendix 2.

Interference tests in this study were carried out at an aluminium concentration of 1.0 ± 0.1 mg/L.

2.5.8.8 Iron

Preparation and standardization of iron stock solution

A stock iron solution of approximately 60 mg/L was prepared from a certified iron standard (BDH Chemicals, Toronto, Ont) and was standardized by GFAAS. The instrument parameters and the conditions used in the analysis can be found in Appendix 2.

Interference tests in this study were carried out at an added iron concentration of 0.6 ± 0.1 mg/L.

2.5.8.9 Monochloramine (as Cl_2)

Several methods have been reported in the literature[62,104,105] for the preparation of monochloramine. For the purposes of this work the method outlined by Gordon[62] was used to prepare working stock solutions of this species.

The conversion of hypochlorous acid (or hypochlorite) to monochloramine in the presence of excess ammonia is rapid and virtually quantitative providing sufficient care is taken in the procedure. The rate of the reaction and the end-products produced are both pH dependent . The optimum pH for the formation of monochloramine (NH_2Cl) is 8 to 8.5[17]. The reaction requires excess ammonia or ammonium ion (generally ammonium chloride is used) to ensure that all the chlorine species present is converted to the required product.

Preparation of stock solution. The reagents used in this study were ammonium chloride (Anachemia, Montreal, Que) and sodium hypochlorite obtained by dilution of a solution of commercial bleach. The ammonium chloride was buffered with standard phosphate buffer (Fisher Scientific, Nepean, Ont) and the pH of this solution was adjusted to 8.3 with sodium hydroxide. Dilute hypochlorite was then slowly added, with constant stirring to the ammonium chloride solution, which was present in a 3:1 molar excess. The resulting solution of monochloramine was stored at 4°C in a refrigerator until required. This solution will remain stable for several days at this temperature provided the pH of the solution is kept relatively constant.

Standardization. Monochloramine can be standardized by any method which is used for the analysis of chlorine. In this case the initial step of the Aieta method (step A) was used to determine the concentration of the stock solution. The same procedure outlined earlier for the standardization of hypochlorous acid and hypochlorite was followed. Stock solutions of 200 ± 5 mg/L (as chlorine) were prepared and interference tests using an added concentration of 2 ± 0.2 mg/L of monochloramine (as chlorine) were done. Triplicate analyses were carried out for all experiments

2.5.8.10 Dichloramine (as Cl_2)

Preparation of stock solution. Dichloramine ($NHCl_2$) can readily be prepared from a stock solution of freshly prepared monochloramine by adjusting the pH of the monochloramine solution to 5 with 2M hydrochloric acid[62]. The acid must be added slowly and with constant stirring. The reaction is relatively slow and takes 3 to 4 hours to complete. The progress of the reaction can be monitored spectrophotometrically by following the absorption maximum of dichloramine at around 297 nm ($\varepsilon = 265\ M^{-1}\ cm^{-1}$)[98]. Dichloramine solutions are unstable and should be used immediately after preparation and standardization.

Standardization. The standardization procedure was as described earlier for monochloramine. Interference testing was carried out in triplicate at the same levels as for monochloramine (2 ± 0.2 mg/L as chlorine).

2.5.8.11 Calcium (as $CaCO_3$)

Calcium in drinking water contributes to the hardness of the water. A calcium standard was prepared as follows:

Preparation of stock solution. A stock solution of approximately 1000 mg/L was prepared by weighing (to the nearest 0.1 mg) 1g of anhydrous calcium carbonate and transferring it into a 500-mL beaker. A sufficient amount (5 to 10 mL) of 6M hydrochloric acid was then added dropwise to completely dissolve the calcium carbonate. To this solution was added with constant stirring 300 mL of distilled water and the solution boiled for 10 to 15 minutes while stirring on a hot plate to expel all remaining carbon dioxide. The heat was then turned off and the solution allowed to cool to room temperature. A few drops of 0.01% methyl red indicator was added to the solution, followed by dropwise addition of 3M ammonium hydroxide until the original red solution turned yellow. The solution was then carefully adjusted with hydrochloric acid and/or ammonium hydroxide until the intermediate orange color of the indicator was produced. At this point the pH of the solution was between 5 and 6, the required range. The solution was then transferred quantitatively to a 1-L volumetric flask and diluted to volume with distilled water.

Standardization. A 50-mL aliquot of a 10 fold dilution of the stock solution prepared above was pipetted into a 250-mL erlenmeyer flask. The pH of the sample was raised to 12 by the addition of 2 to 3 mL of 1.0 M sodium hydroxide and a sufficient amount (0.1 to 0.2 g) of Eriochrome Blue Black R (Anachemia, Montreal, Que) was added. The resulting pink solution was then titrated with standard 0.01 M

EDTA to a purple end point. Several replicate determinations were carried out to ensure good reproducibility. The concentration of calcium in mg/L as $CaCO_3$ is calculated from the equation previously given in chapter 1 of this thesis (see section on calcium hardness determination).

Interference tests in this study were carried out at a calcium concentration of 100 ± 5 mg/L (as $CaCO_3$).

2.5.8.12 Copper

Preparation and standardization of copper stock solution

A stock solution of approximately 25 mg/L (containing 3% by volume of concentrated nitric acid as a preservative) was prepared from a certified copper standard (BDH Chemicals, Toronto, Ont). This solution was standardized by atomic absorption. The method used was identical to that described for the metals analysis in Chapter 1. The Varian SpectrAA 300-400 AA instrument parameters and the conditions used in the analysis can be found in Appendix 2.

Interference tests in this study were carried out at an added copper concentration of 0.2 ± 0.02 mg/L.

2.5.8.13 Summary of Results

The results of the interference tests are shown in Tables 2.7 to 2.10. The amount of interferent added to the sample solutions was confirmed wherever possible by the preparation and analysis of separate blank solutions that contained only the interferent species prior to each interference test. The effect of each of the species studied on the various methods is summarized in the following discussion:

Chloride, the final decomposition product for several chlorine containing species present in drinking water (including chlorine dioxide and chlorite ion), appears to have little effect on any of the analytical methods studied in this work. It does not absorb at

Table 2.7

Interference Data Summary for the UV Method for Chlorine Dioxide.

(a) 0.1± 0.05 mg/L

Interferent Species	Interferent concentration	ClO_2 standard concentration	ClO_2 standard + interferent	Net Effect of Interferent
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Chloride ion	6.2 ± 0.3	0.111 ± 0.003	0.117 ± 0.003	+ 0.006 ± 0.004
Chlorite ion	6.9 ± 0.3	0.113 ± 0.006	0.113 ± 0.006	0 ± 0.008
Chlorate ion	3.9 ± 0.3	0.111 ± 0.003	0.111 ± 0.006	0 ± 0.007
Hypochlorous Acid	2.0 ± 0.1	0.111 ± 0.003	0.110 ± 0.003	- 0.001 ± 0.004
Hypochlorite	2.0 ± 0.1	0.110 ± 0.003	0.118 ± 0.006	+ 0.008 ± 0.007
Aluminium	1.0 ± 0.1	0.103 ± 0.006	0.101 ± 0.003	- 0.002 ± 0.007
Iron	0.6 ± 0.1	0.126 ± 0.003	0.113 ± 0.005	- 0.013 ± 0.006
Monochloramine	2.0 ± 0.2	0.144 ± 0.006	0.146 ± 0.006	+ 0.002 ± 0.008
Dichloramine	2.0 ± 0.2	0.151 ± 0.005	0.147 ± 0.006	- 0.004 ± 0.007
Calcium	100 ± 5	0.146 ± 0.006	0.148 ± 0.003	+ 0.002 ± 0.007
Copper	0.2 ± 0.02	0.144 ± 0.006	0.148 ± 0.003	+ 0.004 ± 0.007

(b) 0.6 ± 0.05 mg/L

Interferent Species	Interferent concentration	ClO_2 standard concentration	ClO_2 standard + interferent	Net Effect of Interferent
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Chloride ion	6.2 ± 0.3	0.604 ± 0.006	0.596 ± 0.006	- 0.008 ± 0.008
Chlorite ion	6.9 ± 0.3	0.606 ± 0.012	0.604 ± 0.006	- 0.002 ± 0.013
Chlorate ion	3.9 ± 0.3	0.604 ± 0.006	0.606 ± 0.003	+ 0.002 ± 0.007
Hypochlorous Acid	2.0 ± 0.1	0.636 ± 0.006	0.638 ± 0.003	+ 0.002 ± 0.007
Hypochlorite	2.0 ± 0.1	0.636 ± 0.006	0.633 ± 0.003	- 0.003 ± 0.004
Aluminium	1.0 ± 0.1	0.609 ± 0.006	0.602 ± 0.006	- 0.007 ± 0.008
Iron	0.6 ± 0.1	0.581 ± 0.008	0.563 ± 0.013	- 0.018 ± 0.015
Monochloramine	2.0 ± 0.2	0.595 ± 0.003	0.593 ± 0.006	- 0.002 ± 0.007
Dichloramine	2.0 ± 0.2	0.602 ± 0.008	0.591 ± 0.003	- 0.011 ± 0.008
Calcium	100 ± 5	0.620 ± 0.006	0.617 ± 0.003	- 0.003 ± 0.007
Copper	0.2 ± 0.02	0.628 ± 0.009	0.621 ± 0.006	- 0.007 ± 0.010

Table 2.8

Interference Data Summary for the Aieta Method for Chlorine Dioxide.

(a) 0.1± 0.05 mg/L

Interferent Species	Interferent concentration	ClO_2 std concentration	ClO_2 std + interferent	Net Effect of Interferent
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Chloride ion	6.2 ± 0.3	0.096 ± 0.002	0.092 ± 0.008	- 0.004 ± 0.008
Chlorite ion	4.2 ± 0.3	0.125 ± 0.001	0.095 ± 0.061	- 0.030 ± 0.061
Chlorate ion	3.9 ± 0.3	0.096 ± 0.002	0.096 ± 0.003	0 ± 0.004
Hypochlorous Acid	2.0 ± 0.1	0.145 ± 0.011	0.138 ± 0.011	- 0.007 ± 0.015
Hypochlorite	2.0 ± 0.1	0.103 ± 0.011	0.093 ± 0.016	- 0.010 ± 0.019
Aluminium	1.0 ± 0.1	0.079 ± 0.001	0.077 ± 0.003	- 0.002 ± 0.003
Iron	0.6 ± 0.1	0.115 ± 0.004	0.127 ± 0.007	+ 0.012 ± 0.008
Monochloramine	2.0 ± 0.2	0.099 ± 0.003	0.101 ± 0.006	+ 0.002 ± 0.007
Dichloramine	2.0 ± 0.2	0.110 ± 0.007	0.119 ± 0.017	+ 0.009 ± 0.018
Calcium	100 ± 5	0.108 ± 0.003	0.118 ± 0.003	+ 0.010 ± 0.004
Copper	0.2 ± 0.02	0.148 ± 0.010	0.180 ± 0.024	+ 0.032 ± 0.026

(b) 0.6 ± 0.05 mg/L

Interferent Species	Interferent concentration	ClO_2 std concentration	ClO_2 std + interferent	Net Effect of Interferent
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Chloride ion	6.2 ± 0.3	0.629 ± 0.018	0.635 ± 0.010	+ 0.006 ± 0.020
Chlorite ion	4.2 ± 0.3	0.635 ± 0.010	0.601 ± 0.070	- 0.034 ± 0.071
Chlorate ion	3.9 ± 0.3	0.628 ± 0.018	0.636 ± 0.006	+ 0.008 ± 0.020
Hypochlorous Acid	2.0 ± 0.1	0.602 ± 0.004	0.610 ± 0.002	+ 0.008 ± 0.005
Hypochlorite	2.0 ± 0.1	0.612 ± 0.013	0.595 ± 0.015	- 0.017 ± 0.019
Aluminium	1.0 ± 0.1	0.630 ± 0.012	0.614 ± 0.008	- 0.016 ± 0.014
Iron	0.6 ± 0.1	0.581 ± 0.030	0.623 ± 0.013	+ 0.042 ± 0.032
Monochloramine	2.0 ± 0.2	0.630 ± 0.014	0.629 ± 0.015	- 0.001 ± 0.020
Dichloramine	2.0 ± 0.2	0.587 ± 0.029	0.571 ± 0.021	- 0.016 ± 0.036
Calcium	100 ± 5	0.545 ± 0.031	0.540 ± 0.041	- 0.005 ± 0.051
Copper	0.2 ± 0.02	0.586 ± 0.020	0.602 ± 0.023	+ 0.016 ± 0.031

Table 2.9

Interference Data Summary for the ACVK Method for Chlorine Dioxide.

(a) 0.1± 0.05 mg/L

Interferent Species	Interferent concentration	ClO_2 std concentration	ClO_2 std + interferent	Net Effect of Interferent
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Chloride ion	6.2 ± 0.3	0.109 ± 0.003	0.111 ± 0.006	+ 0.002 ± 0.007
Chlorite ion	3.5 ± 0.3	0.124 ± 0.001	0.123 ± 0.008	- 0.001 ± 0.008
Chlorate ion	3.9 ± 0.3	0.106 ± 0.004	0.116 ± 0.002	+ 0.010 ± 0.004
Hypochlorous Acid	2.0 ± 0.1	0.105 ± 0.010	0.115 ± 0.003	+ 0.010 ± 0.009
Hypochlorite	2.0 ± 0.1	0.110 ± 0.006	0.112 ± 0.005	+ 0.002 ± 0.008
Aluminium	1.0 ± 0.1	0.115 ± 0.002	0.117 ± 0.005	+ 0.002 ± 0.005
Iron	0.6 ± 0.1	0.114 ± 0.006	0.093 ± 0.008	- 0.021 ± 0.010
Monochloramine	2.0 ± 0.2	0.108 ± 0.011	0.102 ± 0.008	- 0.006 ± 0.013
Dichloramine	2.0 ± 0.2	0.100 ± 0.005	0.091 ± 0.005	- 0.009 ± 0.007
Calcium	100 ± 5	0.118 ± 0.005	0.109 ± 0.005	- 0.009 ± 0.007
Copper	0.2 ± 0.02	0.116 ± 0.004	0.113 ± 0.006	- 0.003 ± 0.007

(b) 0.6 ± 0.05 mg/L

Interferent Species	Interferent concentration	ClO_2 std concentration	ClO_2 std + interferent	Net Effect of Interferent
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Chloride ion	6.2 ± 0.3	0.585 ± 0.013	0.596 ± 0.019	+ 0.011 ± 0.023
Chlorite ion	3.5 ± 0.3	0.550 ± 0.007	0.544 ± 0.003	- 0.006 ± 0.008
Chlorate ion	3.9 ± 0.3	0.585 ± 0.013	0.593 ± 0.004	+ 0.008 ± 0.014
Hypochlorous Acid	2.0 ± 0.1	0.645 ± 0.013	0.635 ± 0.022	- 0.010 ± 0.025
Hypochlorite	2.0 ± 0.1	0.628 ± 0.024	0.618 ± 0.018	- 0.010 ± 0.030
Aluminium	1.0 ± 0.1	0.659 ± 0.013	0.650 ± 0.022	- 0.009 ± 0.026
Iron	0.6 ± 0.1	0.604 ± 0.016	0.562 ± 0.026	- 0.042 ± 0.030
Monochloramine	2.0 ± 0.2	0.624 ± 0.013	0.620 ± 0.009	- 0.004 ± 0.016
Dichloramine	2.0 ± 0.2	0.610 ± 0.025	0.600 ± 0.019	- 0.010 ± 0.019
Calcium	100 ± 5	0.556 ± 0.015	0.572 ± 0.013	+ 0.016 ± 0.019
Copper	0.2 ± 0.02	0.624 ± 0.013	0.634 ± 0.016	+ 0.010 ± 0.020

Table 2.10

Interference Data Summary for the CPR Method for Chlorine Dioxide.

(a) 0.1 ± 0.05 mg/L

Interferent Species	Interferent concentration	ClO_2 std concentration	ClO_2 std + interferent	Net Effect of Interferent
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Chloride ion	6.2 ± 0.3	0.114 ± 0.004	0.113 ± 0.001	- 0.001 ± 0.004
Chlorite ion	1.5 ± 0.2	0.115 ± 0.001	0.078 ± 0.004	- 0.037 ± 0.004
Chlorate ion	3.9 ± 0.3	0.114 ± 0.004	0.112 ± 0.002	- 0.002 ± 0.004
Hypochlorous Acid	2.0 ± 0.1	0.117 ± 0.002	0.130 ± 0.002	+ 0.013 ± 0.003
Hypochlorite	2.0 ± 0.1	0.134 ± 0.002	0.148 ± 0.001	+ 0.014 ± 0.002
Aluminium	1.0 ± 0.1	0.115 ± 0.003	0.117 ± 0.002	+ 0.002 ± 0.004
Iron	0.6 ± 0.1	0.114 ± 0.002	0.113 ± 0.003	- 0.001 ± 0.004
Monochloramine	2.0 ± 0.2	0.126 ± 0.003	0.126 ± 0.004	0 ± 0.005
Dichloramine	2.0 ± 0.2	0.115 ± 0.005	0.116 ± 0.003	+ 0.001 ± 0.006
Calcium	100 ± 5	0.124 ± 0.003	0.122 ± 0.003	- 0.002 ± 0.004
Copper	0.2 ± 0.02	0.138 ± 0.003	0.140 ± 0.002	+ 0.002 ± 0.004

(b) 0.6 ± 0.05 mg/L

Interferent Species	Interferent concentration	ClO_2 std concentration	ClO_2 std + interferent	Net Effect of Interferent
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Chloride ion	6.2 ± 0.3	0.576 ± 0.023	0.570 ± 0.009	- 0.006 ± 0.024
Chlorite ion	1.5 ± 0.2	0.582 ± 0.002	0.563 ± 0.008	- 0.019 ± 0.008
Chlorate ion	3.9 ± 0.3	0.576 ± 0.023	0.577 ± 0.010	+ 0.001 ± 0.025
Hypochlorous Acid	2.0 ± 0.1	0.621 ± 0.011	0.681 ± 0.009	+ 0.060 ± 0.014
Hypochlorite	2.0 ± 0.1	0.599 ± 0.013	0.650 ± 0.016	+ 0.051 ± 0.021
Aluminium	1.0 ± 0.1	0.635 ± 0.003	0.624 ± 0.013	- 0.011 ± 0.013
Iron	0.6 ± 0.1	0.617 ± 0.004	0.615 ± 0.005	- 0.002 ± 0.006
Monochloramine	2.0 ± 0.2	0.651 ± 0.008	0.639 ± 0.013	- 0.012 ± 0.015
Dichloramine	2.0 ± 0.2	0.594 ± 0.013	0.604 ± 0.003	+ 0.010 ± 0.013
Calcium	100 ± 5	0.573 ± 0.008	0.566 ± 0.005	- 0.007 ± 0.009
Copper	0.2 ± 0.02	0.592 ± 0.005	0.598 ± 0.008	+ 0.006 ± 0.009

360 nm, is not titrated in the Aieta method, and does not react with either CPR or ACVK. Therefore it can be concluded that the presence of chloride ion in solution does not pose any problems to the analysis of chlorine dioxide by the methods studied.

Chlorite ion, one of two major decomposition products of chlorine dioxide (chlorate is the other), has no significant effect on either the UV or ACVK methods. Since chlorite ion is determined in steps 2 and 4 in the Aieta method, it is not strictly an inteference in this method. As previously stated in the discussion on the comparison of the UV and Aieta methods, however, the level of chlorite ion in the sample has a significant effect on the concentration of chlorine dioxide determined by the Aieta method. Because chlorine dioxide is determined by difference, the determination of small amounts in the presence of larger amounts of chlorite ion is subject to error in the Aieta procedure. This difficulty can be seen from Table 2.8, and should be borne in mind when this analysis is carried out.

Chlorite ion also appears to have some effect on the CPR method, since the presence of chlorite ion produces lower results in the analysis of chlorine dioxide than is found in the standards. Since chlorite ion does not (in the authors experience) react directly with CPR it is possible that some reaction involving chlorite ions and chlorine dioxide is taking place in solution, although at present the nature of such a reaction is unclear. The possibility that chlorine dioxide could be reacting with an impurity in the sodium chlorite used to prepare the stock solution is unlikely because an assay provided with the chlorite, 90.1% as sodium chlorite, revealed nothing that would be expected to react directly with chlorine dioxide. Since the level of chlorite ion added to the samples in this study was considerably greater than would normally be expected in drinking water, however, chlorite ion is not expected to be a major interferent in the CPR method for real samples.

Chlorate ion is a relatively inert species that does not appear to be an interferent for any of the methods studied. It is determined by an extension to the Aieta procedure but under the conditions normally used for this method it does not interfere.

Hypochlorous acid is determined in step 1 (and also after nitrogen purging in step 3) of the Aieta method. Since it is titrated and removed from solution it is not an interference in this method. It also is not an interference in either the ACVK or UV methods. Hypochlorous acid does, however, give a false positive test with CPR as has been reported previously[71] and is a definite interference in this method. The ACVK method is carried out between pH 8 and 9, a range within which HOCl is almost entirely converted to OCl^-. As a result of this hypochlorous acid will not interfere with this method. In the Edmonton water treatment procedure all hypochlorous acid initially present is converted into chloramines (predominantly monochloramine) and therefore should not be present in the finished drinking water.

Hypochlorite ion (OCl^-) has interference properties similar to those of hypochlorous acid. It is an inteference in the CPR method because in the pH range over which the reaction is carried out, 5.2 to 5.5, most of the hypochlorite is converted to hypochlorous acid. The same points given above for hypochlorous acid in the Aieta method also apply here. As can be seen from Figure 28, hypochlorite is not an interferent in the ACVK method.

Aluminium, which is present in the City of Edmonton drinking water in concentrations up to 1 mg/L[100], does not appear to be a serious interferent for any of the methods at the level tested (1 mg/L) in this study.

Iron at the 0.6 mg/L level appears to interfere to some extent in the UV, Aieta, and ACVK methods, but does not appear to have any effect on the CPR method.

Aqueous solutions of Fe^{3+} ion have some residual absorbance at 360 nm which interferes in the UV method. This can largely be compensated for by measuring the absorbance of blank solutions containing only iron and then sample solutions containing iron and chlorine dioxide. The blank absorbance is then subtracted from that of the sample to obtain the absorbance due to the sample alone. This correction is feasible provided the concentration of iron is known or is determined by an independent method.

For the Aieta method higher chlorine dioxide concentrations were observed in the samples containing both iron and chlorine dioxide than in the chlorine dioxide standards alone. Iron (III), like several other species such as copper (II) and manganese (IV), can oxidize iodide to iodine under favorable conditions, such as low pH values. These conditions exist in steps 2 and 4 of the Aieta method, where chlorite ion and chlorine dioxide are reduced. Hence additional titratable iodine is produced in these steps and higher results are obtained as a consequence.

Iron is also a minor interference in the ACVK method. Slightly lower values were obtained for the samples than for the standards, indicating that chlorine dioxide is reacting with iron. The observed interference is relatively small, however, and the concentration of iron added in this study was of the order of 30 to 40 times that normally found in most drinking water.

Monochloramine (NH_2Cl), which is formed in City of Edmonton drinking water from ammonia and chlorine, serves as a secondary disinfectant for the distribution system. It is considerably less reactive towards many compounds[106] than the free chlorine species (HOCl and OCl^-), does not react with either ACVK or CPR, and behaves in a similar manner to free chlorine in the Aieta method. As a result monochloramine is not considered to be an interferent for any of the analytical methods studied.

Dichloramine ($NHCl_2$) also does not appear to interfere significantly in any of the methods. In the pH range at which the ACVK method is carried out (8 to 9) it is likely that dichloramine is converted to monochloramine because the equilibrium between these compounds is pH dependant. Under conditions normally used in water treatment, it is likely that little or no dichloramine is produced.

Calcium does not appear to interfere in any of the methods in this study. It is normally present, generally as the sulfate or bicarbonate, in drinking water at a concentration of 60 to 70 mg/L (as $CaCO_3$) and is an integral part of the hardness component of the water.

Copper (II) is an interferent in the Aieta method because at low pH it oxidizes iodide to iodine according to the reaction:

$$2\,Cu^{2+} + 4\,I^- = Cu_2I_2 + I_2$$

However, in normal drinking water samples the level of copper is generally in the range of only 0.001 to 0.010 mg/L and as a result would not be expected to interfere to any significant extent. Copper does not appear to interfere in any of the other three methods studied.

The results of these tests indicate that at the levels studied the majority of these species do not significantly interfere with any of the methods.

The UV method, which was only used to standardize chlorine dioxide solutions, appears to be essentially free of interferences from these species.

The Aieta method has several interferences. The presence in solution of any species capable of oxidizing iodide to iodine, such as Cu^{2+} or Fe^{3+}, is particularly likely to produce errors. As stated previously, the determination of low concentrations of chlorine dioxide in the presence of higher concentration of chlorite ions is difficult with this method and subject to large errors. Since this situation often occurs in real samples, it constitutes a major drawback to the method.

However, the various forms of chlorine and chloramines are not interferents in the Aieta method. Indeed, as shown, it can be utilized to standardize stock solutions of several chlorine species. Therefore this method has some utility in that respect.

With the exception of a minor interference from iron (III) the ACVK method appears to be essentially free of interferences from the species studied and therefore applicable to the analysis of real drinking water samples.

Free chlorine and, to a lesser extent, chlorite ion interfere in the chlorophenol red (CPR) method. Chlorine is not present in City of Edmonton drinking water in significant amounts. Chloramines, which are present, do not interfere. It therefore seemed possible that the chlorophenol red method also might be adopted for the analysis of chlorine dioxide in drinking water in which chloramines are used. But CPR as already mentioned has several drawbacks.

The next part of this work, therefore, describes the investigation of a number of related indicators as possible alternatives to CPR and ACVK. Our goal was to develop a colorimetric procedure along the lines of the ACVK method to field test against already existing methods for the analysis of drinking water.

2.5.9 Alternative Indicators For Chlorine Dioxide Determination

2.5.9.1 Introduction

The ACVK method developed by Masschelein[72,73] has, as previously stated, two major advantages over the CPR method. The first is that it requires only one reagent, which makes it easier to use in the field; the second is that it is applicable in the normal pH range encountered in drinking water samples. This is in contrast to the CPR method, which requires two buffers to adjust the pH of the sample. A major disadvantage to the ACVK method, however, is that it is relatively insensitive. The absorbtivity of ACVK, as measured in this work is 11.30 ± 0.15 L g^{-1} cm^{-1} (average of four replicate determinations). Note that absorbtivity rather than molar absorbtivity is reported here.

Absorbtivity (α) is defined as the absorbance of a substance divided by the product of the concentration of that substance and the sample path length. When the concentration is in units of g/L and the path length is in cm, the units of absorbtivity (α) are L g^{-1} cm^{-1}. In this work absorbtivities were calculated instead of the more usual molar absorbtivity coefficients (ε) because the majority of the indicators studied were not available in pure form and hence molar concentrations of these species could not be accurately specified.

The low absorbtivity of ACVK meant that changes in absorbance at low concentrations of chlorine dioxide were small. This limited the minimum concentration which could be reliably detected by this method to 0.02 ± 0.01 mg/L[71] of chlorine dioxide. The CPR method on the other hand has an observed detection limit of less than 0.01 mg/L[71] due to the considerably higher absorbtivity (approximately 90 L g^{-1} cm^{-1}) of chlorophenol red.

However, because of the advantages stated above for the ACVK method we were interested in also investigating a number of other dyes as possible replacements for ACVK.

ACVK, [1, 5-bis-(4-methylphenylamino-2-sodium sulfonate)-9, 10-anthraquinone] has a symmetrical structure with five benzene rings. Substituents on the various rings include two methyl groups, two sodium sulfonate groups to provide water solubility, and two ketone functions. In addition the molecule contains two sites where a pair of benzene rings are joined via an N-H linkage, which breaks the conjugation of the molecule at these two points. ~~In~~ general terms, as the degree of conjugation (an unbroken sequence of alternating single and multiple bonds) in a molecule increases, it absorbs light at longer wavelengths. Conjugation also infers a number of other properties for a molecule, one being an increase in thermodynamic stability[107]. In addition, an increase in the degree of conjugation in a molecule will usually result in a higher molar absorbtivity coefficient.

In considering possible alternative indicators to ACVK, a number of properties are desirable. These include:

(a) It should react with chlorine dioxide in a rapid, quantitative, and reproducible manner.

(b) It should have a high absorbtivity.

(c) It should not react with other chlorine species, especially oxychlorine species present in solution (i.e it must be interference free). This would not be tested in the initial screening, but at a later stage for selected compounds which showed promise.

(d) It must be water soluble.

In addition, because it is necessary to prepare buffered (pH 9-10) solutions of the indicator (as in the ACVK method), we also wanted the species to form a stable solution at about that pH range.

A large number of compounds were considered as potential alternatives. Since we required the molecule to have a high absorbtivity (which implies a high degree of conjugation) many of these species contained large aromatic ring systems. But the requirement of water solubility limited the size of the ring system. We also wished to avoid highly substituted molecules because of possible interferences, and molecules containing reactive substituent groups. We also did not consider molecules containing other halogen atoms such as bromine or iodine to avoid potential interference problems.

In all 13 compounds were selected for this study. These included several species having N-H linkages similar to ACVK (such as Alizarin Blue Black B), and a number of azo compounds (such as Acid Black 24). Since chlorine dioxide is an electrophilic species the nitrogen atoms (which have lone pairs of electrons associated with them) are potential reaction sites for oxidation by chlorine dioxide. The experimental procedure followed in testing each compound was essentially identical, and is described in the following sections.

Experimental Work. All indicators used in this work with the exception of amaranth, which was obtained from Matheson, Coleman, and Bell (Norwood, Ohio), were purchased from the Aldrich Chemical Company (Milwaukee, Wis). Buffered solutions of the indicators were prepared in pure water as described by Masschelein[73] at a nominal concentration of 2×10^{-4} M. Standard calibration curves were determined and plotted in duplicate over a range of concentration from 0 to 0.5 mg/L of chlorine dioxide for all indicators studied. Six standards were prepared over this range. Chlorine dioxide stock solutions were prepared from sodium chlorite and acetic anhydride as described earlier, and dilute standards in the relevant range were standardized using the UV method described previously. The procedure for the construction of the calibration curves was as follows:

Procedure. Chlorine dioxide standard solutions were prepared in 250-mL volumetric flasks. For each point on the curve three standards of the required concentration were prepared by dilution of a more concentrated standard of known concentration. These dilute standards were then analyzed in triplicate by the UV method, using a 10-cm path length cell to determine the exact concentration of chlorine dioxide present.

A second set of three identical chlorine dioxide standards of the same concentration was then prepared along with a blank solution containing distilled water only. To each of these solutions a 10-mL aliquot of buffered indicator solution was added via a 10-mL volumetric pipet and the solutions inverted several times to mix. The absorbances of all four solutions were then measured (also in triplicate) with a 10-cm cell (a 2-cm cell was used for evans blue) at the wavelength of maximum absorbance for the particular compound being investigated. From these measurements the average absorbance of the three standards and the blank was evaluated using three replicate absorbances, and the change in absorbance (blank absorbance minus sample absorbance) determined for each standard by subtracting the average absorbance for the blank from that obtained for each standard.

Standard calibration curves of the change in absorbance against the chlorine dioxide concentration were then plotted and absorbtivities calculated. An example of a calibration curve (for amaranth) is shown in Table 2.11.

To check reproducibility a second identical solution of the compound was prepared, two additional calibration curves plotted, and two more absorbtivities calculated. The data obtained for the calibration curves and the absorbtivities for both solutions was then compared. For the majority of compounds good agreement was obtained for the two solutions. When there was some discrepancy (generally in the absorbtivity values) a third solution of the compound was prepared and the work repeated. All solutions were stored in dark bottles in a refrigerator at 4°C until required.

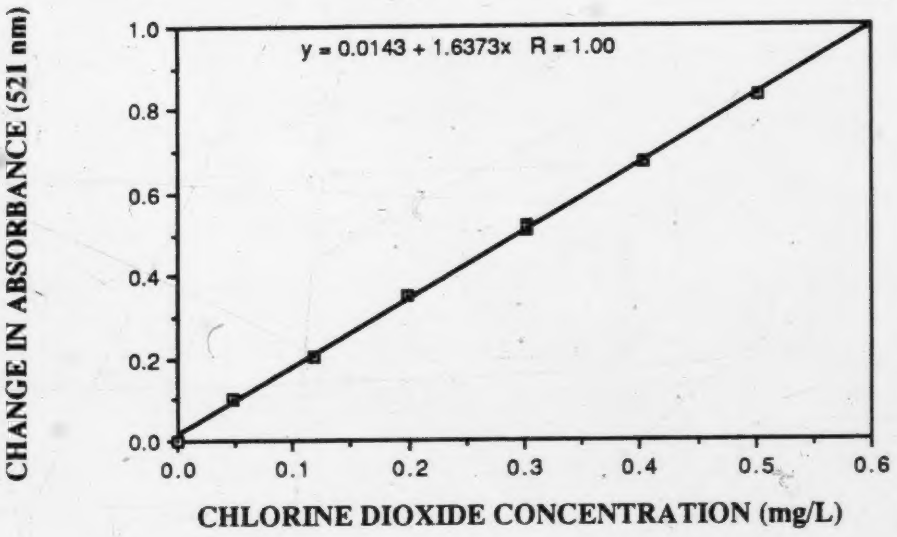
To assess the stability of the indicator solutions the following procedure was carried out. A 10-mL aliquot was pipetted into a 250-mL volumetric flask, diluted to volume,

Table 2.11

Calibration Curve Data and Calibration Graph for Amaranth.

0 to 0.5 mg/L

Std No	Chlorine Dioxide Concentration	Sample Absorbance (521 nm)	Blank Absorbance (521 nm)	Change In Absorbance (521 nm)
	(mg/L)			
1	0.048 ± 0.011	1.675 ± 0.004	1.777 ± 0.002	0.102 ± 0.005
2	0.117 ± 0.008	1.580 ± 0.005	1.781 ± 0.002	0.201 ± 0.006
3	0.199 ± 0.011	1.427 ± 0.006	1.781 ± 0.004	0.352 ± 0.007
4	0.302 ± 0.006	1.264 ± 0.005	1.780 ± 0.001	0.516 ± 0.005
5	0.403 ± 0.008	1.109 ± 0.004	1.781 ± 0.002	0.672 ± 0.005
6	0.502 ± 0.006	0.948 ± 0.009	1.778 ± 0.004	0.829 ± 0.010



and the absorbance measured (in triplicate) at the wavelength of maximum absorbance using a 10-cm path length cell. This procedure was repeated once a day for a period of one week [illegible] the majority of cases the solutions of the various compounds were found to be stable and could be stored for up to a month with little change in absorbance.

The results obtained for the individual indicators will now be discussed. Chemical structures for these compounds are shown on pages 125 to 128.

2.5.9.2 Amaranth[108] (I)

Formula Weight (F.Wt) = 604.48 g

λmax = 521 nm

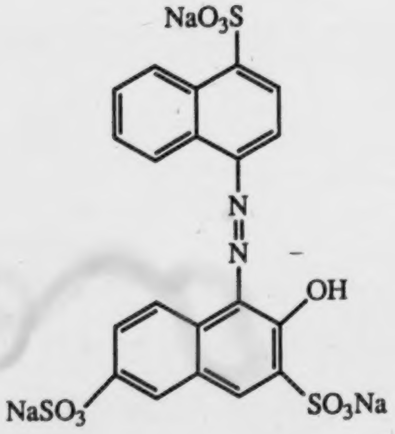
Color Index (CI) = 16185

% purity = Not available (100% assumed)

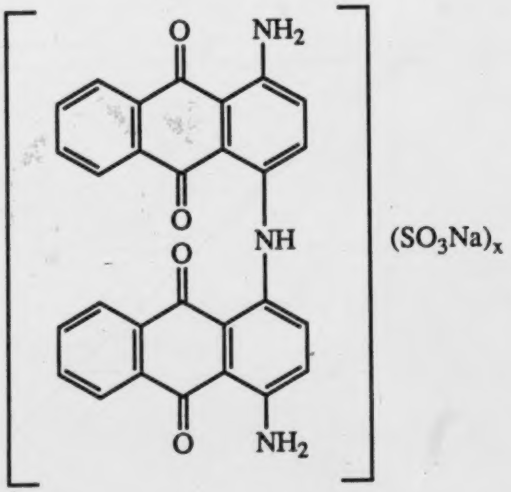
Lot Number = E5L 24

Preparation of stock solution. A stock solution (nominally 2 x 10^{-4} M) of amaranth was prepared by weighing (to the nearest 0.1 mg) 0.1212 g of the compound into a 150-mL beaker. This was dissolved in 80 mL of distilled water and transferred quantitatively to a 1-L volumetric flask. To the flask was then added 48.5 g of ammonium chloride (Anachemia, Montreal, Que) which had previously been dissolved in 200 mL of distilled water, 20 mg of sodium hexametaphosphate (Aldrich Chemical Co, Milwaukee, Wis) and 10 mL of concentrated ammonium hydroxide (Allied Chemical Co, Pointe Claire, Que). The ammonium chloride and the ammonia form the components of the pH 9-10 buffer solution. The flask was diluted to volume with distilled water and a magnetic stirring bar was then added to the flask. The solution was stirred for a period of 24 hours, transferred to a dark glass bottle and stored in a refrigerator until required.

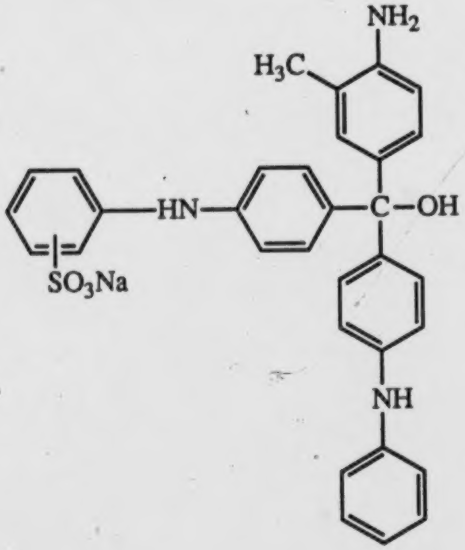
(I). AMARANTH



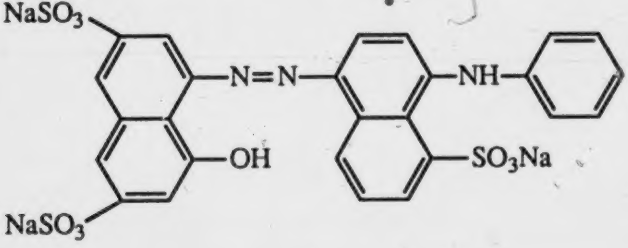
(II). ACID BLACK 48



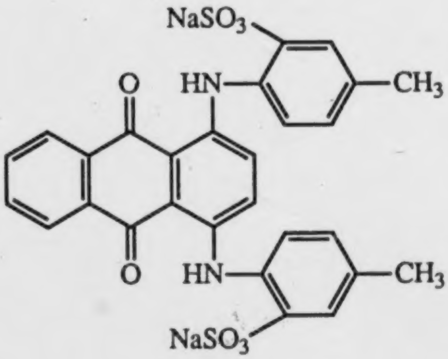
(III). ALKALI BLUE 6B



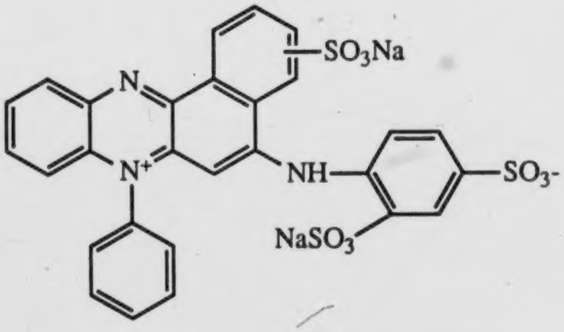
(IV). ACID BLUE 92


NaSO3
N=N
NH
OH
SO3Na
NaSO3

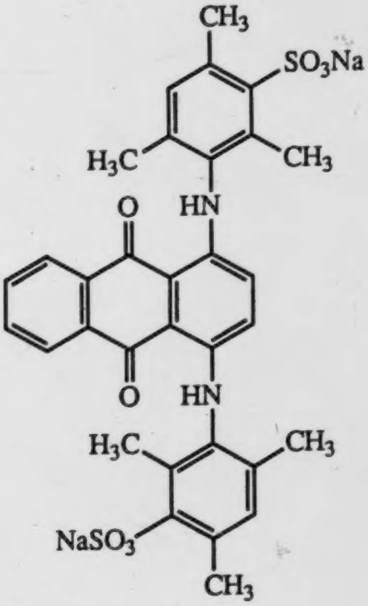
(V). ACID GREEN 25


NaSO3
O
HN
CH3
O
HN
CH3
NaSO3

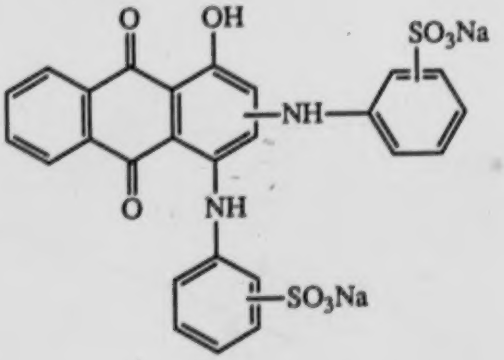
(VI). AZOCARMINE B


SO3Na
N
N+
NH
SO3-
NaSO3

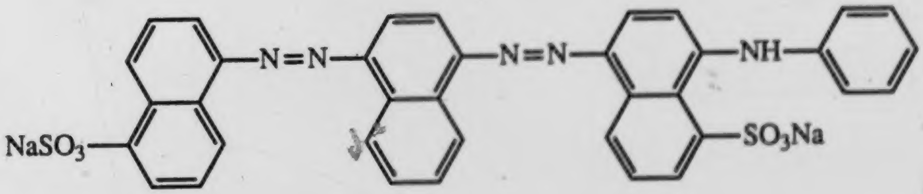
(VII). ACID BLUE 80


CH3
SO3Na
H3C
CH3
O
HN
O
HN
H3C
CH3
NaSO3
CH3

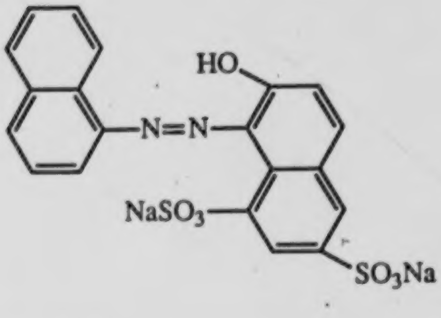
(IX). ALIZARIN BLUE BLACK B


O
OH
SO3Na
NH
O
NH
SO3Na

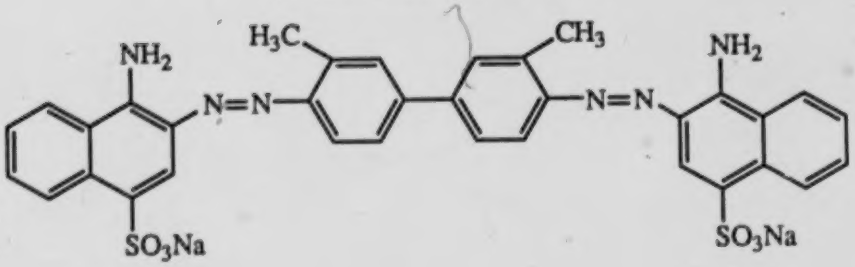
(VIII). ACID BLACK 24


N=N
N=N
NH
NaSO3
SO3Na

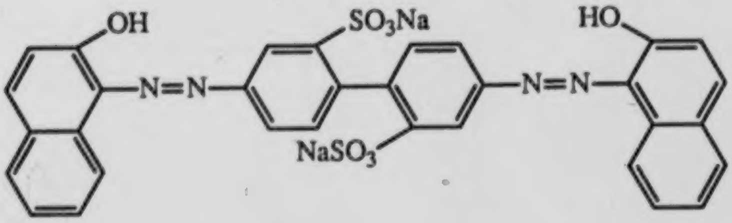
(X). CRYSTAL SCARLET


HO
N=N
NaSO3
SO3Na

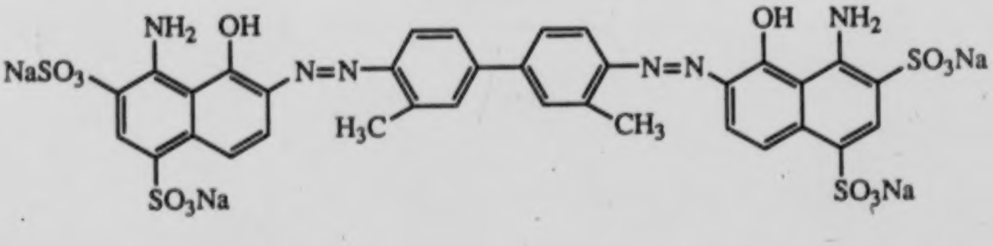
(XI). BENZOPURPURIN 4B


NH2
H3C
CH3
NH2
N=N
N=N
SO3Na
SO3Na

(XII). ACID RED 97


OH
SO3Na
HO
N=N
N=N
NaSO3

(XIII). EVANS BLUE


NH2
OH
OH
NH2
NaSO3
N=N
N=N
SO3Na
H3C
CH3
SO3Na
SO3Na

Procedure. The procedure followed in preparing the buffered stock solutions for all the other indicators was identical to the above. The weight of each indicator taken was sufficient to prepare a nominally 2 x 10^{-4} M solution. Therefore details of the preparation of the indicator stock solutions will not be included in the remainder of this discussion of the individual compounds.

Amaranth is decolorized by chlorine dioxide within 30 seconds. The average value of the absorbtivity calculated for amaranth was 38.09 ± 0.46 L g^{-1} cm^{-1} (based on four replicate measurements). This value is approximately three and a half times that calculated for ACVK. Hence amaranth should be more sensitive to chlorine dioxide than ACVK on a gram for gram basis, that is, the observed change in absorbance for amaranth should be about three and a half times greater than that of ACVK for the same concentration of chlorine dioxide Amaranth is also very soluble in water due to the presence of three sulfonate groups on the molecule, and calibration curves (see procedure described earlier) are linear and reproducible (see Table 2.11). In addition, buffered solutions of amaranth are extremely stable. From these preliminary results this compound was selected for further study as a potential alternative to ACVK.

2.5.9.3 Acid Black 48 (II)

Formula Weight (F.Wt) = Not available (number of sulfonate groups unknown)

λmax = 663 nm

Color Index (CI) = 65005

% purity = approximately 40 %

Lot Number (Aldrich) = AX 0032277

In preparing the stock solution the formula weight of acid black 48 was calculated as 599 assuming two sodium sulfonate (SO_3Na) groups are present in the molecule. Acid black 48 is soluble in water and is decolorized by chlorine dioxide to give a linear calibration curve over the range of the standards studied. The calculated value of the average absorbtivity, 8.45 ± 0.15 L g^{-1} cm^{-1} (based on four replicates), however, is less than the value calculated for ACVK (11.30 ± 0.15 L g^{-1} cm^{-1}). Therefore this compound is less sensitive to chlorine dioxide than ACVK. A comparison of plots of change in absorbance against concentration of chlorine dioxide showed this to be the case. Also solutions of this compound degrade on standing with formation of a precipitate. For these reasons Acid Black 48 was not considered further.

2.5.9.4 Alkali Blue 6B (III)

Formula Weight (F.Wt) = 573.65
λmax = 603 nm
Color Index (CI) = 42750
% purity = approximately 90 %
Lot Number (Aldrich) = AX 88521 PM

Although alkali blue is decolorized by chlorine dioxide and gives a linear calibration curve, it is somewhat insoluble in water, yields variable absorbtivity values, and its solutions appear to be light sensitive. In overall sensitivity it is comparable to ACVK (plots of the change in absorbance against concentration for the two species are virtually identical), but the instability of its solutions eliminated it from further consideration.

2.5.9.5 Acid Blue 92[109] (IV)

Formula Weight (F.Wt) = 695 59
λmax = 571 nm
Color Index (CI) = 13390
% purity = approximately 40 %
Lot Number (Aldrich) = PV 01513 CT

This compound is rapidly decolorized by chlorine dioxide and calibration curves plotted over the range of the standards are linear and reproducible. The average absorbtivity calculated for this compound was 28.50 ± 0.28 L g^{-1} cm^{-1} (based on four replicates). In terms of sensitivity acid blue 92 is approximately three times more sensitive to chlorine dioxide than ACVK. Solutions of acid blue 92 were found to be stable and so from initial work this compound merits further consideration as a possible alternative to ACVK.

2.5.9.6 Acid Green 25 (V)

Formula Weight (F.Wt) = 622.59

λmax = 642 (608) nm

Color Index (CI) = 61570

% purity = approximately 75 %

Lot Number (Aldrich) = DX 02422 JP

Acid green 25 is decolorized rapidly by chlorine dioxide and the resulting calibration curves are linear and reproducible over the range covered by the standards. The average absorbtivity calculated for this compound was 19.48 ± 0.21 L g^{-1} cm^{-1} making it approximately one and a half times more sensitive than ACVK. Although solutions of this compound are stable the overall increase in sensitivity was not considered sufficient to warrant further attention.

2.5.9.7 Azocarmine B (VI)

Formula Weight (F.Wt) = 681.63

λmax = 516 nm

Color Index (CI) = 50090

% purity = approximately 80 %

Lot Number (Aldrich) = HW 12630 AW

This compound gave a calculated average absorbtivity of 39.83 ± 0.16 L g^{-1} cm^{-1} (based on four replicates) and like amaranth is approximately three and a half times more sensitive to chlorine dioxide than ACVK. In addition it fulfilled many of the other requirements (such as solution stability, and solubility properties) that are necessary for it to be considered as a possible alternative indicator.

2.5.9.8 Acid Blue 80 (VII)

Formula Weight (F.Wt) = 678.70

λmax = 625 (580) nm

Color Index (CI) = 61585

% purity = approximately 70 %

Lot Number (Aldrich) = PW 01018 ET

Despite the fact that this compound is approximately twice as sensitive to chlorine dioxide as ACVK (the average absorbtivity of acid blue 80 was 24.50 ± 1.49 L g^{-1} cm^{-1} (four replicates)) this compound cannot be considered as a potential alternative to ACVK because calibration curves were not reproducible on a day to day basis, and buffered solutions of the indicator were found to be unstable.

2.5.9.9 Acid Black 24 (VIII)

Formula Weight (F.Wt) = 731.72

λmax = 572 nm

Color Index (CI) = 26370

% purity = approximately 50 %

Lot Number (Aldrich) = DV 0031397

This compound has a calculated average absorbtivity of 12.07 ± 0.26 L g^{-1} cm^{-1} (based on four replicates), which is approximately the same as ACVK. In terms of sensitivity towards chlorine dioxide there is little to choose between the two compounds (acid black 24 is slightly the more sensitive of the two). Despite its complex structure it is very soluble in water and buffered solutions of the compound were found to be stable. Considering the relatively high degree of conjugation present the lack of enhanced sensitivity was somewhat disappointing, and the compound was not considered further.

2.5.9.10 Alizarin Blue Black B (IX)

Formula Weight (F.Wt) = 610.53

λmax = 548 nm

Color Index (CI) = 63615

% purity = not stated (100% asumed)

Lot Number (Aldrich) = LW 02120 ML

This compound has a similar structure to ACVK and essentially similar properties. The calculated average absorbtivity for alizarin blue black B is 14.51 ± 0.40 L g^{-1} cm^{-1} (based on four replicates) which, although slightly greater than that for ACVK, is slightly inferior in terms of sensitivity towards chlorine dioxide. For this reason it was not considered further.

2.5.9.11 Crystal Scarlet (X)

Formula Weight (F.Wt) = 502.44

λmax = 510 nm

Color Index (CI) = 16250

% purity = approximately 80%

Lot Number (Aldrich) = BX 10122 LT

This compound has both a similar structure and similar absorbtivity to amaranth. The average absorbtivity for crystal scarlet is 40.27 ± 0.43 L g^{-1} cm^{-1} (based on four replicate measurements), whereas that for amaranth is 38.09 ± 0.46 L g^{-1} cm^{-1} (also based on four replicates). Like amaranth, crystal scarlet is soluble in water and buffered solutions are stable. Its sensitivity to chlorine dioxide is not as great as that of amaranth however.

2.5.9.12 Benzopurpurin 4B[110] (XI)

Formula Weight (F.Wt) = 724.73

λmax = 500 nm

Color Index (CI) = 23500

% purity = not stated (100% assumed)

Lot Number (Aldrich) = CT 00320 PL

The calculated average absorbtivity for this compound is 27.94 ± 0.51 L g^{-1} cm^{-1} (based on four replicate measurements) and standard calibration curves obtained for this compound are linear and highly reproducible. But although more sensitive to chlorine dioxide than ACVK by a factor of two, it is inferior to several other compounds already investigated, such as amaranth and azocarmine B.

2.5.9.13 Acid Red 97 (XII)

Formula Weight (F.Wt) = 698.65

λmax = 498 nm

Color Index (CI) = 22890

% purity = approximately 40%

Lot Number (Aldrich) = EW 0032097

This compound, although possessing a highly conjugated structure has a calculated average absorbtivity of only 24.84 ± 0.28 L g^{-1} cm^{-1} (based on six replicate measurements). It is, however approximately three and a half times more sensitive to chlorine dioxide than ACVK and so is comparable to amaranth and azocarmine B in this respect. Calibration curves were reproducible and solutions of the buffered indicator are very stable. Along with the other two compounds mentioned above it should be considered as a potential alternative indicator.

2.5.9.14 Evans Blue[111] (XIII)

Formula Weight (F.Wt) = 960.82

λmax = 611 nm

Color Index (CI) = 23860

% purity = approximately 85%

Lot Number (Aldrich) = EW 01016 CM

This large and highly substituted molecule was the last of the compounds tested in this study. The calculated average absorbtivity, 86.50 ± 0.90 L g^{-1} cm^{-1} (based on four replicate determinations), is more than double that of any of the other compounds tested previously. Thus it is about a factor of ten times more sensitive to chlorine dioxide than ACVK. Despite its size it is readliy soluble in water. Calibration curves were highly reproducible, and solutions of the buffered indicator were very stable.

2.5.9.15 Summary

Of the compounds tested in this screening study evans blue appeared to be the best choice as a possible alternative to ACVK, and further work seemed advisable.

Of the 13 compounds tested, four showed promise as alternatives to ACVK. These four were amaranth, azocarmine B, acid red 97, and evans blue. Although these compounds were superior in terms of sensitivity, it was necessary to do a set of interference tests similar to those already done for the other methods earlier in this work before they could be considered acceptable. Interference testing is laborious and time consuming, and so it was decided to carry out interference studies on two compounds only.

Although evans blue was an obvious choice because of its high sensitivity, the choice of the second compound was not so clear cut. In terms of sensitivity there was little to choose among the other three, and all were soluble and stable in solution. In addition, none contained structural features such as the presence of potentially reactive ring substituents which could be considered a potential problem as regards reactivity with other species in solution. After further consideration it was decided to select amaranth as the second compound. The other two were held in reserve for study if serious interference problems were encountered with amaranth. The details of the second set of interference trials will be discussed in the next section.

2.5.10 Interference Testing on Amaranth and Evans Blue

2.5.10.1 Introduction

The species selected for a study of possible interferences were identical to those described in the first set of tests (see section 2.5.8) except that dichloramine was omitted because at the pH of the City of Edmonton drinking water, 7.5-8.5, this species is not likely to be present to any extent (see earlier). Concentrations of the species tested were essentially the same as before, with some minor differences in chloride and chlorate.

Procedure. The test procedure was identical to that described earlier for the ACVK and CPR colorimetric methods. Each species was tested in standard solutions containing 0.1 ± 0.05 and 0.4 ± 0.05 mg/L of chlorine dioxide respectively. The preparation and standardization of the test species were identical to those described earlier, with the exception of the preparation of monochloramine. This was prepared by a simple and rapid method discovered by the author during the course of this work and is described in the summary part of this section which follows.

2.5.10.2 Results and Discussion of Individual Species Interference Testing

The levels of the various interferent species tested in this second study are shown in Tables 2.12 and 2.13, which contain a summary of the results obtained for amaranth and evans blue.

Chloride appears to have little effect on either amaranth and evans blue at the level tested in this work, 7.6 ± 0.3 mg/L, which is of the order of two to three times the concentration which would normally be found in the City of Edmonton drinking water.

Chlorite, which is also an oxidant, is a minor interference for both amaranth and evans blue. The presence of chlorite ion produces slightly higher results in analyses of chlorine dioxide than is found in the standards. Since the level of chlorite ion added was considerably greater than would normally be expected in drinking water, chlorite ion is not expected to be an interferent for either of these indicators in real samples.

Chlorate, which as stated earlier is relatively inert does not appear to interfere with either indicator at the level tested in this study.

Hypochlorous acid and hypochlorite ion, collectively referred to as "free chlorine", do not interfere significantly with either of the indicators. As stated earlier, little or no free chlorine exists in Edmonton drinking water because it is converted to chloramines (essentially monochloramine) by reacting with ammonia which is added to the water for this purpose.

Aluminium, which is present in the City of Edmonton drinking water at a range of concentrations from 0.3 to 1 mg/L, is an interference for evans blue but not for amaranth. For evans blue higher results were obtained for samples than for standards, which would seem to indicate that aluminium is capable of reacting with the indicator. Experiments were carried out at two levels of added aluminium, 0.5 and 1.0 mg/L, to

Table 2.12

Interference Data Summary For Amaranth.

(a) 0.1 ± 0.05 mg/L Chlorine Dioxide

Interferent Species	Interferent concentration (mg/L)	ClO_2 std concentration (mg/L)	ClO_2 std + interferent (mg/L)	Net Effect of Interferent (mg/L)
Chloride ion	7.6 ± 0.3	0.107 ± 0.001	0.107 ± 0.002	0 ± 0.002
Chlorite ion	3.4 ± 0.3	0.106 ± 0.001	0.114 ± 0.005	+ 0.008 ± 0.005
Chlorate ion	9.8 ± 0.5	0.113 ± 0.005	0.109 ± 0.002	- 0.004 ± 0.005
Hypochlorous Acid	2.0 ± 0.2	0.109 ± 0.002	0.113 ± 0.004	+ 0.004 ± 0.004
Hypochlorite	2.0 ± 0.2	0.111 ± 0.004	0.102 ± 0.004	- 0.009 ± 0.006
Aluminium	1.0 ± 0.1	0.102 ± 0.005	0.098 ± 0.007	- 0.004 ± 0.009
Iron	0.6 ± 0.1	0.107 ± 0.003	0.096 ± 0.006	- 0.011 ± 0.007
Monochloramine	2.0 ± 0.2	0.111 ± 0.004	0.105 ± 0.007	- 0.006 ± 0.008
Calcium	100 ± 5	0.107 ± 0.003	0.106 ± 0.005	- 0.001 ± 0.006
Copper	0.1 ± 0.02	0.111 ± 0.007	0.090 ± 0.005	- 0.021 ± 0.009

(b) 0.4 ± 0.05 mg/L Chlorine Dioxide

Interferent Species	Interferent concentration (mg/L)	ClO_2 std concentration (mg/L)	ClO_2 std + interferent (mg/L)	Net Effect of Interferent (mg/L)
Chloride ion	7.6 ± 0.3	0.400 ± 0.001	0.403 ± 0.003	+ 0.003 ± 0.003
Chlorite ion	3.4 ± 0.3	0.400 ± 0.004	0.423 ± 0.005	+ 0.023 ± 0.006
Chlorate ion	9.8 ± 0.5	0.409 ± 0.003	0.404 ± 0.004	- 0.005 ± 0.005
Hypochlorous Acid	2.0 ± 0.2	0.397 ± 0.008	0.405 ± 0.004	+ 0.008 ± 0.009
Hypochlorite	2.0 ± 0.2	0.405 ± 0.024	0.397 ± 0.018	- 0.008 ± 0.009
Aluminium	1.0 ± 0.1	0.404 ± 0.002	0.390 ± 0.003	- 0.014 ± 0.004
Iron	0.6 ± 0.1	0.406 ± 0.005	0.379 ± 0.006	- 0.027 ± 0.008
Monochloramine	2.0 ± 0.2	0.408 ± 0.006	0.407 ± 0.004	- 0.001 ± 0.007
Calcium	100 ± 5	0.409 ± 0.006	0.411 ± 0.004	+ 0.002 ± 0.007
Copper	0.1 ± 0.02	0.406 ± 0.008	0.362 ± 0.006	- 0.044 ± 0.010

Table 2.13

Interference Data Summary For Evans Blue.

(a) 0.1± 0.05 mg/L Chlorine Dioxide

Interferent Species	Interferent concentration	ClO_2 std concentration	ClO_2 std + interferent	Net Effect of Interferent
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Chloride ion	7.6 ± 0.3	0.110 ± 0.007	0.103 ± 0.004	- 0.007 ± 0.008
Chlorite ion	3.4 ± 0.3	0.102 ± 0.006	0.110 ± 0.005	+ 0.008 ± 0.008
Chlorate ion	9.8 ± 0.5	0.119 ± 0.006	0.115 ± 0.011	- 0.004 ± 0.013
Hypochlorous Acid	2.0 ± 0.2	0.108 ± 0.004	0.118 ± 0.002	+ 0.010 ± 0.004
Hypochlorite	2.0 ± 0.2	0.111 ± 0.007	0.100 ± 0.003	- 0.011 ± 0.008
Aluminium	1.0 ± 0.1	0.104 ± 0.007	0.119 ± 0.005	+ 0.015 ± 0.009
Iron (1)	0.6 ± 0.1	0.121 ± 0.004	0.162 ± 0.010	+ 0.041 ± 0.011
(2)	0.12 ± 0.02	0.115 ± 0.006	0.121 ± 0.006	+ 0.006 ± 0.008
Monochloramine	2.0 ± 0.2	0.109 ± 0.008	0.098 ± 0.002	- 0.011 ± 0.008
Calcium	100 ± 5	0.108 ± 0.008	0.109 ± 0.004	+ 0.001 ± 0.009
Copper	0.1 ± 0.02	0.110 ± 0.006	0.112 ± 0.008	+ 0.002 ± 0.010

(b) 0.4 ± 0.05 mg/L Chlorine Dioxide

Interferent Species	Interferent concentration	ClO_2 std concentration	ClO_2 std + interferent	Net Effect of Interferent
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Chloride ion	7.6 ± 0.3	0.398 ± 0.004	0.403 ± 0.005	+ 0.005 ± 0.006
Chlorite ion	3.4 ± 0.3	0.383 ± 0.008	0.399 ± 0.005	+ 0.016 ± 0.009
Chlorate ion	9.8 ± 0.5	0.395 ± 0.006	0.399 ± 0.007	+ 0.004 ± 0.009
Hypochlorous Acid	2.0 ± 0.2	0.394 ± 0.009	0.392 ± 0.014	- 0.002 ± 0.016
Hypochlorite	2.0 ± 0.2	0.402 ± 0.006	0.392 ± 0.005	- 0.010 ± 0.008
Aluminium	1.0 ± 0.1	0.399 ± 0.010	0.446 ± 0.012	+ 0.047 ± 0.015
Iron (1)	0.6 ± 0.1	0.407 ± 0.008	0.489 ± 0.024	+ 0.082 ± 0.025
(2)	0.12 ± 0.02	0.404 ± 0.009	0.412 ± 0.007	+.0.008 ± 0.011
Monochloramine	2.0 ± 0.2	0.402 ± 0.012	0.397 ± 0.011	- 0.005 ± 0.016
Calcium	100 ± 5	0.410 ± 0.008	0.407 ± 0.005	- 0.003 ± 0.009
Copper	0.1 ± 0.02	0.400 ± 0.011	0.407 ± 0.016	+ 0.007 ± 0.019

determine the extent of this interference. At a level of 0.5 mg/L of added aluminium the interference is negligible and is therefore not expected to be a major problem for the analysis of drinking water samples, but at 1 mg/L the interference is moderate (see Table 2.13).

Iron (III) appears to be an interference for both of the indicators studied, but is a much more serious interference for evans blue than for amaranth. Considerably higher results were obtained for samples than for standards. Similar experiments were carried out as with aluminium with solutions containing added levels of 0.6 and 0.1 mg/L iron respectively. At 0.1 mg/L interference was negligible, but at 0.6 mg/L it was significant. Since the normal concentration of iron in Edmonton drinking water samples is in the range of 0.001 to 0.008 mg/L, iron is not expected to be a major interferent.

Monochloramine, which is used as a secondary disinfectant in the distribution system, does not appear to interfere significantly with either reagent at the 2 mg/L level. Stock solutions of this species were prepared by the addition of a three-fold molar excess of ammonium ion, in the form of solid ammonium chloride, to a solution of hypochlorite prepared as described earlier. The reaction is complete within seconds and gives an essentially quantitative yield of monochloramine.

Calcium does not appear to interfere with either indicator at the level of 100 ± 5 mg/L tested in this work.

Copper (II) appears to interfere with amaranth. High results are obtained for samples at added levels of 0.1 ± 0.02 mg/L of copper. The normal level of copper found in Edmonton drinking water samples is, however, only 0.001 to 0.010 mg/L so it should not be an interferent in the analysis of real samples.

From the above the predominant interferents for amaranth and evans blue are metal ions. Since these metals, with the exception of aluminium, are typically present in city of Edmonton drinking water in only trace amounts they should not present a problem.

2.5.11 Analysis of Chlorine Dioxide in Distribution System Samples

Having completed interference tests for all four colorimetric reagents (ACVK, CPR, amaranth, and evans blue), the next step was to collect and analyze a number of samples from various parts of the distribution system for chlorine dioxide with these reagents.

The initial step was to analyze samples collected from City reservoirs and fire halls, where chlorine dioxide is expected to be absent. These measurements would give an indication of whether the reagents, particularly amaranth and evans blue, would yield false positive values on real samples. The procedure for the analysis was as follows.

Procedure. For each of the indicators a 0 to 0.5 mg/L calibration curve was prepared using finished water from Rossdale reservoir (#1 plant) which had essentially the same composition as the samples. For the purposes of this study it was assumed that all the distribution system samples were homogeneous (from the results obtained in the sampling study carried out earlier (see chapter 1) this appears to be a reasonable assumption). Analysis of each of the samples was carried out in triplicate and the concentration of chlorine dioxide was determined from standard calibration plots of change in absorbance against concentration. The results are shown in Table 2.14. Uncertainties in the data represent one standard deviation.

From these results two conclusions can be drawn. Firstly, it appears that the level of chlorine dioxide in the distribution system is negligible. As stated earlier this result was not altogether unexpected as several papers have drawn attention to the fact that chlorine dioxide is rapidly converted to chlorite ion, chlorate ion, and chloride ion[54],

Table 2.14

Results for Determination of Chlorine Dioxide (in mg/L) In the City of Edmonton Water Distribution System in September 1990 by Four Spectrophotometric Methods.

Spectrophotometric Reagent

Sample Origin	Date	Acid Chrome Violet K	Chlorophenol Red	Amaranth	Evans Blue
Thorn-cliff	Sept 20 th	0.008 ± 0.002	0.002 ± 0.001	0.000 ± 0.001	0.006 ± 0.001
North Jasper	Sept 20 th	0.007 ± 0.002	0.004 ± 0.001	0.004 ± 0.001	0.003 ± 0.001
Rosslyn #1	Sept 21 st	0.005 ± 0.002	0.002 ± 0.000	0.003 ± 0.001	0.003 ± 0.001
Clare-view	Sept 21 st	0.006 ± 0.004	0.003 ± 0.000	0.005 ± 0.000	0.003 ± 0.000
London-derry	Sept 21 st	0.007 ± 0.004	0.004 ± 0.001	0.005 ± 0.000	0.005 ± 0.001
# 2 Fire Hall	Sept 22 nd	0.006 ± 0.004	0.002 ± 0.001	0.003 ± 0.001	0.005 ± 0.001
# 5 Fire Hall	Sept 22 nd	0.009 ± 0.004	0.003 ± 0.000	0.006 ± 0.001	0.005 ± 0.000

during the disinfection process. Secondly, since the absorbances obtained for the distribution system samples were essentially the same as those obtained in distilled water, no species present in the drinking water samples appears to be present at a concentration level sufficient to interfere with either amaranth or evans blue.

Since no chlorine dioxide was found in the distribution system itself it was decided to study a stage of the drinking water treatment process where ClO_2 was likely to be present. A convenient site is the stilling basins at the Rossdale water treatment plant, in which the chlorine dioxide disinfection process takes place.

2.5.12 Stilling Basin Studies

2.5.12.1 Turbidity Effects

Chlorine dioxide, along with chlorine and fluoride in the form of sodium fluorosilicate, is added directly after the recarbonation stage of the drinking water treatment process (see Figure 1.3). The disinfection process takes place in the stilling basins where the water is allowed sufficient contact time[44] for the disinfection process to be completed. After this process the water passes through a set of anthracite filters, which is the last stage of the process before the water goes to the storage reservoir and from there into the distribution system. The water in the stilling basins possesses the same characteristics as the water in the distribution system, but it contains silt and other suspended material, and is therefore considerably more turbid than normal drinking water samples (the anthracite filtration step removes most of the material responsible for the high turbidity). Also, since the stilling basins are open to the atmosphere the water in the basins is subject to variable environmental conditions.

Preliminary studies[112] by Rossdale treatment plant laboratory personnel in the summer of 1988 indicated that concentrations of chlorine dioxide were highest at the north ends of the basins, nearest the point of application, and tapered to virtually zero by approximately the mid-points of the basins. A boat was used to collect samples at a depth of approximately 2 m below the surface. Chlorine dioxide is destroyed by direct sunlight, and therefore would not be expected to be present for long on or near the surface. The method of analysis used in their work was visible spectrophotometry with chlorophenol red, with the UV method being used as a comparison. Despite the very preliminary nature of the study (for example, the effect of turbidity on the analysis was not adequately taken into account) it did afford useful background information on the distribution of chlorine dioxide in the basins.

Procedure. To assess the effect of sample turbidity on the four colorimetric reagents used in this work, large samples (approximately 10 L) of water were collected at a depth of approximately 1.5 m below the surface from the south end of stilling basin #2. The Rossdale water treatment plant has two identical stilling basins, one each for plants #1 and #2. At this sampling site no chlorine dioxide was expected to be present in the sample; this was verified by the analysis of a portion of the sample (in triplicate) by the Aieta titration procedure described earlier. All samples were collected using a specially designed water sampler which operates on a pulley system. The sampler is lowered into and removed from the body of water by means of ropes. The device can be opened as required below the surface to collect the sample, and then closed again before the sample is brought to the surface. This avoids the possibility of surface films and other debris being collected along with the sample. Several operations were required (the volume of the sampler is 1 to 2 L) to obtain the volume of sample required (10 L) and care was taken to collect the samples from approximately the same location and depth each time. After collection the composite sample was stored in the dark in a 20-L polyethylene carboy until required. The following experimental procedure was carried out to determine the effect of turbidity on the colorimetric reagents studied in this work.

Several pairs of clean, dry 250-mL volumetric flasks were prepared. The sample collected from the stilling basin was first shaken to disperse the silt and other particles evenly throughout the solution, then 250-mL aliquots of the sample water was pipetted into one of the flasks in each pair to serve as a blank. Since no chlorine dioxide was present, addition of sodium thiosulfate to dechlorinate the blank was unneccessary. Experiments were, however, carried out to assess the effect of sodium thiosulfate on the absorbance of solutions containing the reagents used in this study; in all cases it was found that thiosulfate had a negligible effect on the absorbance. Into the second flask of each pair was pipetted 230 mL of sample water, followed by sufficient chlorine dioxide stock solution to prepare a standard of the desired concentration. The flask was then diluted to volume with sample water. The amount of chlorine dioxide added was selected so as to prepare a set of standards in the range of 0 to 0.5 mg/L for amaranth, ACVK, and evans blue.

For chlorophenol red the concentration range covered by the standards was reduced to 0 to 0.25 mg/L, since above this range the calibration curve was nonlinear. The procedure followed was identical to that described earlier for the 0 to 0.15 mg/L calibration curve in the section on the chlorophenol red method, except that the amount of reagent 2 (chlorophenol red solution) was increased from 0.5 to 1.0 mL. Identical sets of solutions were prepared in distilled water so that a direct comparison could be made between the results obtained for distilled and stilling basin water.

After all the flasks were filled to the mark with sample water, the colorimetric reagent(s) were added and the absorbance of each pair of solutions determined, in triplicate, at the appropriate wavelength. A standard calibration curve of the change in absorbance against chlorine dioxide concentration was then plotted for each reagent and water combination as described earlier. The exact concentration of the chlorine dioxide added to the solutions was determined by UV. Replicate calibration curves were then constructed for each by repeating the above procedure to assess reproducibility. The calibration curves were then compared to those obtained for each indicator in distilled water.

Results and discussion

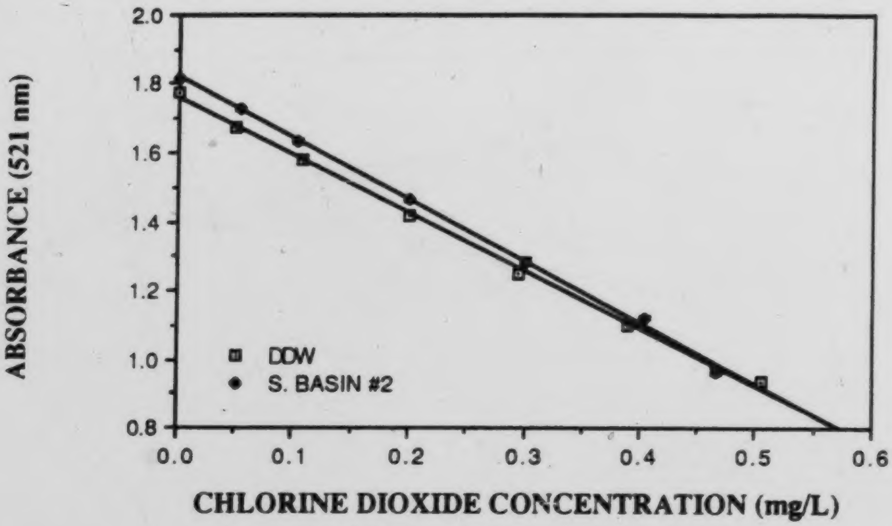
Several observations can be made from the data obtained from these experiments. Firstly, the major effect of increased sample turbidity is to increase the observed absorbance of the solutions. But so long as the degree of turbidity in all the solutions is constant, the net change in absorbance does not differ significantly from that observed in distilled water (assuming that no reaction occurs with the turbid matter). As an example of this consider Figure 2.5 (a) and (b), which shows plots of the absorbance and the change in absorbance for amaranth in distilled and stilling basin water from basin #2 at the Rossdale plant. We can see that the absorbances of the solutions prepared with basin water are slightly higher than those prepared with distilled water, but the changes in absorbance are very similar. Comparable results were obtained for all four of the reagents.

If the turbidity varies from sample to sample then major errors can result. Since the particulate matter which is predominantly responsible for the increased turbidity will eventually settle out over several hours aliquots of sample should be taken in as short a time frame as possible to ensure that the turbidity of all the solutions is approximately equal. If aliquots are taken over a longer period of time while settling is occurring, variable absorbances will be observed and non linear calibration curves will be produced.

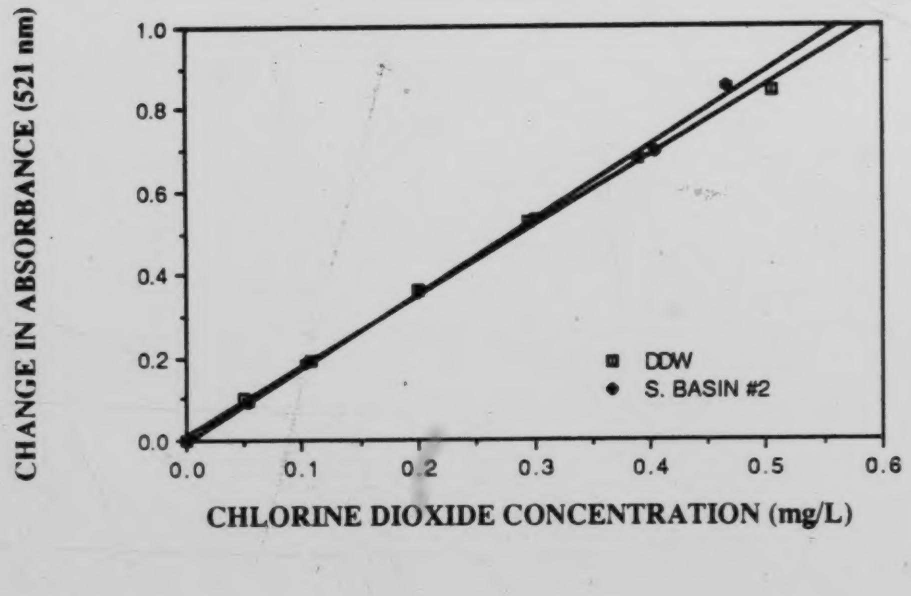
Turbidities of samples obtained from the basins, measured by nephelometry, were found to be in the range of 5 ± 2 NTU (Nephelometric Turbidity Units). This is in

Figure 2.5

(a) Plot of Absorbance Against Added Chlorine Dioxide Concentration for Amaranth in Distilled and Stilling Basin Sample Water.



(b) Plot of the Change in Absorbance Against Added Chlorine Dioxide Concentration for Amaranth in Both Distilled and Stilling Basin Sample Water.



contrast to most drinking water samples where the turbidities are of the order of 0 to 0.5 NTU (see appendix 1). Insofar as possible an attempt was made to ensure that the turbidity was similar for all experiments so that qualitative comparisons of the turbidity effects on individual reagents could be done. In practice this was achieved by taking samples from approximately the same position and depth in the basin (#2), and by measuring the turbidity of the sample (in triplicate) before each experiment.

The effect of increased sample turbidity on evans blue, which has a high absorbtivity and hence a high absorbance, was found to be virtually negligible. That is to say, the absorbances of solutions prepared in distilled and stilling basin water were virtually identical. This is useful knowledge. On the other hand ACVK, which has a low absorbtivity, is particularly sensitive to increased turbidity. The need to maintain the turbidities of the solutions approximately equal is particularly important with this reagent.

Overall, it was found that although additional sample turbidity must be taken into account, it is not an insurmountable problem for the analysis of chlorine dioxide by colorimetric reagents, providing suitable precautions are taken as described above.

In the next stage of this work we wished to study the effect of time and temperature on the four colorimetric reagents studied in this work. For this purpose a set of experiments were designed and carried out using both distilled (millipore) and stilling basin water. Details of these experiments are contained in the next section.

2.5.12.2 Time Effects

Procedure. Experiments designed to determine the relative stability with time of the various solutions containing the colorimetric reagents studied in this work were carried out in screw capped, 250-mL dark glass bottles obtained from the process development team at the E.L Smith water treatment plant in Edmonton. A series of solutions were prepared and analyzed at intervals over a period of three hours. The analysis times were 2, 15, 30, 45, 60, 90, 120, 150, and 180 minutes; all measurements were made within two minutes of the nominal time. Once the solutions had been prepared they were placed in a commercial cooler that held the temperature of the solutions in the range 20 ± 2°C. The temperature of each solution was determined after analysis to ensure that it was within the required limits. Experiments were carried out on both distilled and stilling basin water using a series of solutions having the following compositions: ACVK blank and with 0.3 mg/L of added ClO_2, CPR blank and with 0.2 mg/L of added ClO_2, amaranth blank and with 0.3 mg/L of added ClO_2, and evans blue blank and with 0.3 mg/L of added ClO_2, making a total of sixteen experiments in all (eight in distilled water and eight in stilling basin water). Samples collected from the basin were allowed to stand for a period of 24 hours prior to use to allow the particles contained in the sample to settle. This was done to reduce the turbidity of the sample so it would not be a factor in these experiments and also to allow time for any residual chlorine dioxide present in the sample to decompose. Aliquots were removed by pipetting from the top of the container to avoid disturbing the sediment. All experiments were run in pairs (for example ACVK blank and 0.3 mg/L of ClO_2 in distilled water) so that the change in absorbance for the solutions could be determined under as nearly identical conditions as possible and thus be comparable. The experimental procedure was as follows:

For each experiment 18 clean and dry screw capped 250-mL dark glass bottles were arranged in pairs and labelled. Into each of the bottles designated as blanks in the experiment was pipetted 250 ml of sample water (either distilled or from the stilling basin). The caps were then replaced on each bottle to prevent dust or other particulate matter getting into the solution. A 240-mL aliquot of the same water was then pipetted into each of the sample bottles and the caps replaced. The following set of operations was then carried out for each of the blank and sample pairs. Firstly the colorimetric reagent (or reagents) was added to the blank and the time of addition (T_{add}) was recorded. The relevant quantity of chlorine dioxide (0.2 or 0.3 ppm depending on the reagent being studied) was then added to the sample bottles. The chlorine dioxide standard was prepared so a 10-mL aliquot was equivalent to the required concentration. The total volume of the solution was thus made up to 250 mL, so that it was not necessary to add further sample water to bring the solution to the correct value. The colorimetric reagent (or reagents for CPR) was then added, and the time of addition again recorded; for CPR this corresponded to the time of addition of reagent 3. Both bottles were then inverted to mix and placed in the cooler. Each blank/sample pair was treated in a similar way until all nine had been carried through the process. The blank/sample pairs were then removed from the cooler and analyzed in reverse order, i.e. the last pair to be treated was analyzed first. The absorbance (in triplicate) and the temperature of each solution were recorded. The time at which the first absorbance measurement was recorded was designated the measurement time ($T_{measure}$). The total elapsed time between the addition of the colorimetric reagent and the measurement (T_{total}) was then calculated (in minutes) for each solution using the expression, $T_{measure} - T_{add}$. From this data plots of the change in absorbance against T_{total} were constructed for each blank-sample pair. The uncertainty values on the plots represent one standard deviation. This overall standard deviation was calculated from the individual standard deviations associated with the blank and the sample, using the standard equation given earlier in this Chapter in the initial work on the chlorophenol red method.

Results and discussion

The results obtained for each of the indicators can be summarized as follows;

(a) ACVK

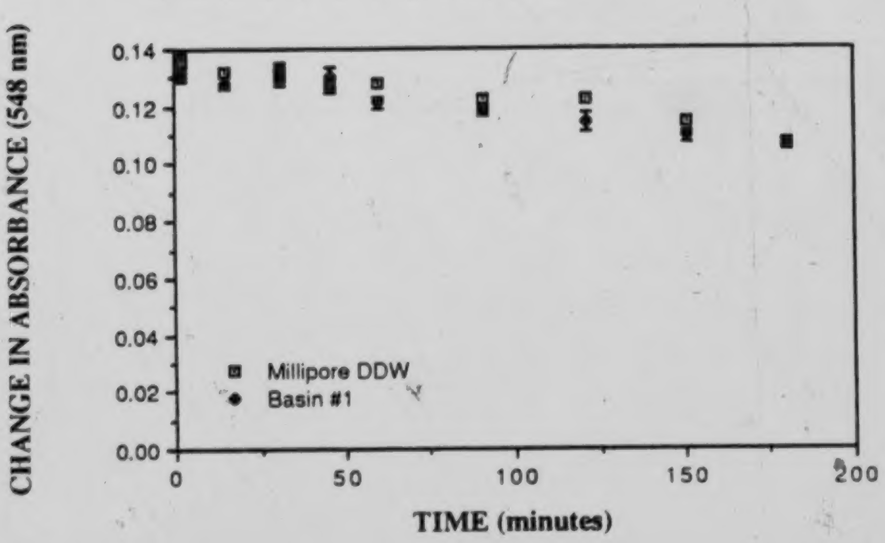
The plots of change in absorbance against time for ACVK in both distilled and stilling basin water (see figure 2.6 a) show a similar trend. Over the duration of the experiment the change in absorbance gradually decreases. This is due to the fact that the absorbance of the samples increases with time while that of the blanks remains virtually constant. The absorbance increase for the sample solutions could be explained by slow reforming of the original ACVK species, or to a rearrangement of the oxidized reagent to another species that absorbs at the wavelength used. Over the first hour of the experiment the observed change in absorbance in distilled water at the wavelength studied, 548 nm, decreased by 0.008 (b = 10 cm). Similar results were obtained for solutions prepared from stilling basin water. In terms of concentration this difference amounts to approximately 0.02 mg/L of chlorine dioxide. From these results it is recommended that measurements with ACVK be made as quickly as possible after sample collection and reagent addition to minimize errors.

(b) Amaranth

From figure 2.6 b we can see that the change in absorbance with time for indicator-chlorine dioxide mixtures over the duration of the experiment (approximately three hours) is relatively small, approximately 0.020 absorbance units in distilled water and 0.030 in stilling basin water (b = 10 cm). As with ACVK, the blanks remain relatively stable while a slight decrease in the change in absorbance, corresponding to a slight increase in absorbance for the samples, was observed. However, amaranth is considerably more sensitive than ACVK and thus a higher change in absorbance is observed for the same concentration of chlorine dioxide. For the calibration curve

Figure 2.6

(a) Plot of Change in Absorbance Against Time for Solutions Containing ACVK in Both Distilled (Millipore) and Stilling Basin Water.



(b) Plot of Change in Absorbance Against Time for Solutions Containing Amaranth in Both Distilled (Millipore) and Stilling Basin Water.

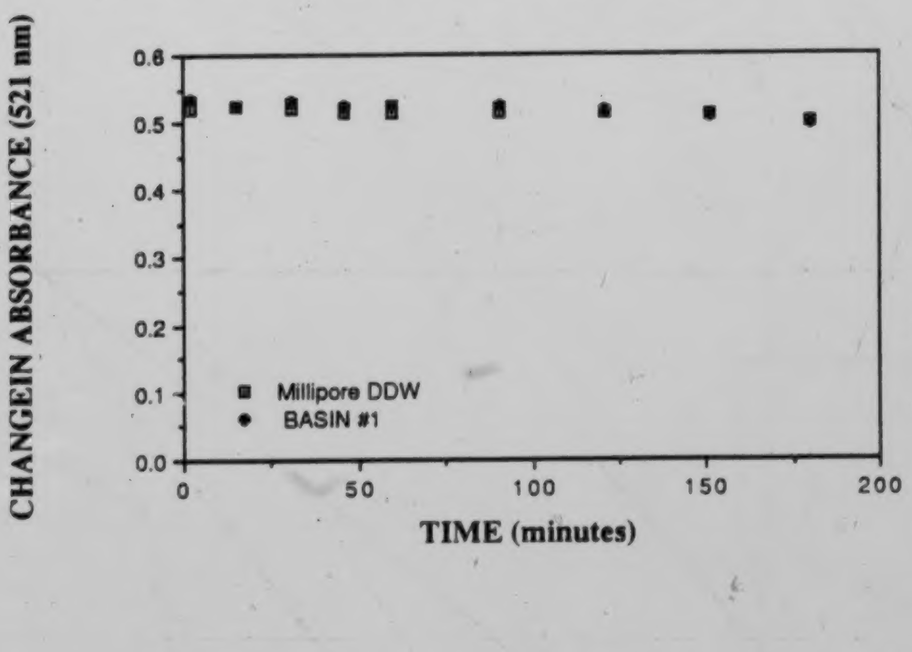
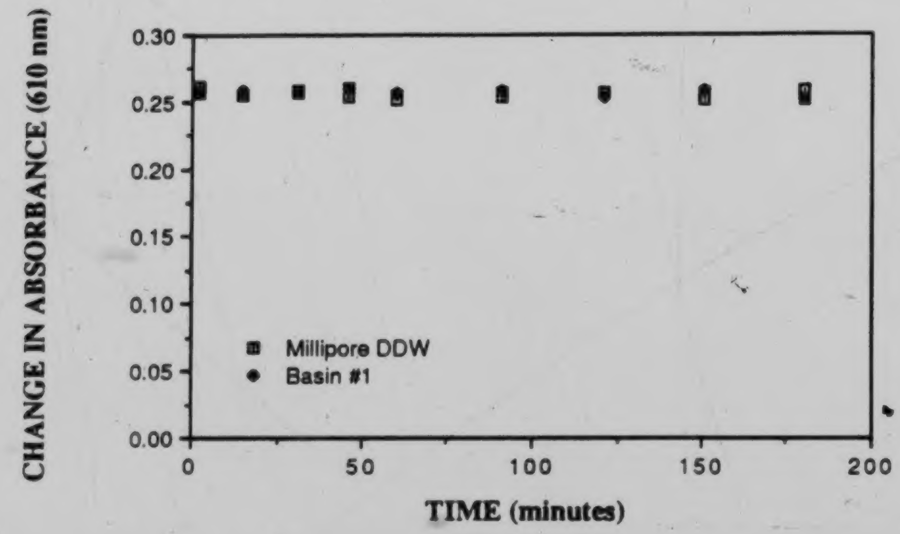
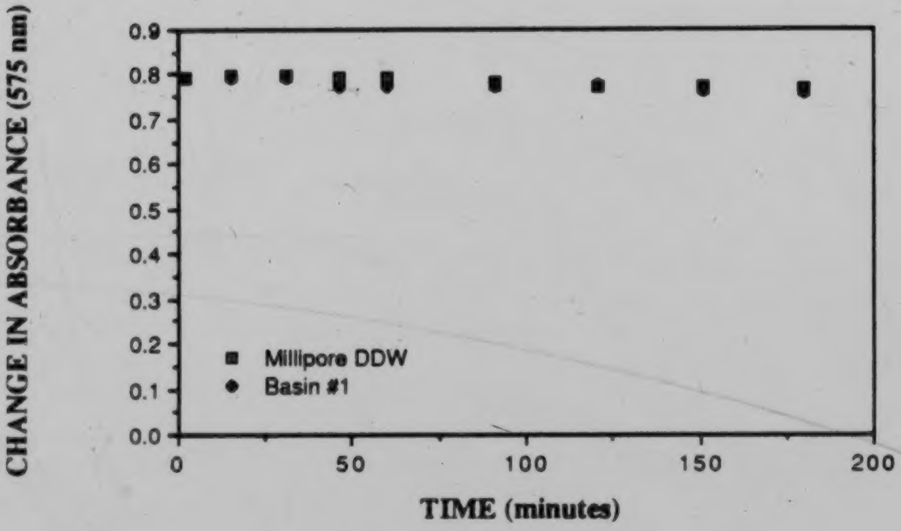


Figure 2.7

(a) Plot of Change in Absorbance Against Time for Solutions Containing Evans Blue in Both Distilled (Millipore) and Stilling Basin Water.



(b) Plot of Change in Absorbance Against Time for Solutions Containing Chlorophenol Red in Both Distilled (Millipore) and Stilling Basin Water.



used, a change in absorbance of 0.018 corresponds to approximately 0.01 mg/L of chlorine dioxide. Over the first hour of the experiment the absorbance readings remained essentially constant in both distilled and basin water. Therefore, for this indicator samples can be stored for at least an hour (at a temperature of 20 ± 2°C) prior to analysis without major bias being incurred.

(c) Evans blue

From figure 2.7 a we can see that the change in absorbance with time for indicator-chlorine dioxide mixtures over the period of the experiment remained virtually unchanged. In both distilled and stilling basin water the observed change in absorbance over the three hour duration of the experiment, approximately 0.007 absorbance units, corresponds to a chlorine dioxide concentration of approximately 0.01 ppm. Therefore this indicator is as stable as amaranth.

(d) Chlorophenol Red (CPR)

From figure 2.7 b we can see that results obtained for CPR are similar to those for amaranth and evans blue. After one hour changes in absorbance of 0.002 and 0.020 absorbance units (b = 10 cm) were observed for distilled and stilling basin water respectively. From the calibration curve, a change in absorbance of 0.040 is equivalent to 0.01 mg/L of ClO_2, so the observed differences represent very small changes in concentration.

To sum up the results of this set of experiments, we can see that of the four compounds only ACVK appears to introduce error if sample-reagent mixtures are allowed to stand longer than 5 to 10 minutes prior to analysis. The other three indicators appear to be stable with time. However, it is recommended that with all these reagents measurements should be made within one hour of sample collection for optimum results.

Additional experiments

Procedure. A second set of experiments was carried out to complement the findings of the initial set. One of each of the solutions described in the previous set was made up. After mixing, a portion of the solution was transferred into a spectrophotometer cell as before and absorbance readings at λ_{max} were taken every 15 minutes for two hours. Although facilities were not available to thermostat the cell compartment of the Shimadzu 160 spectrophotometer used in this work, the temperature of the solution in the cell was measured before being placed in the cell, and again after the experiment. The overall increase in temperature was found to be of the order of 3 to 4°C over the course of the experiment, which was deemed to be acceptable. Since only one spectrophotometer was available, blanks and samples were prepared separately and measured in succession. Care was taken to ensure that all solutions were at approximately the same temperature prior to the measurement step. As before the change in absorbance was determined and plotted against time.

Results. These experiments confirmed the results obtained in the previous experiments. The trends observed in both sets of experiments were identical for all four indicators. Some minor differences in the change in absorbance were obtained, particularly towards the end of the time period of this second set of experiments, which may be due either to the formation of air bubbles in the cell on standing or the effect of variations in the temperature of the cell contents over time.

However, the reason for the observed increase in absorbance with time for solutions containing chlorine dioxide and ACVK at 548 nm remained unsolved. Therefore a further experiment was carried out on this indicator. A blank solution containing ACVK only was prepared, a portion of the solution was transferred to a 10-cm cell, and the visible spectrum between 400 and 800 nm was recorded with the Shimadzu 160 spectrophotometer. A second solution containing ACVK and 0.3 mg/L of ClO_2 was then prepared and the spectrum of this solution was recorded over the same wavelength range as above. A further scan of the spectrum of this solution was taken every 15 minutes for a period of two hours. The results obtained from this experiment are shown in Figure 2.8.

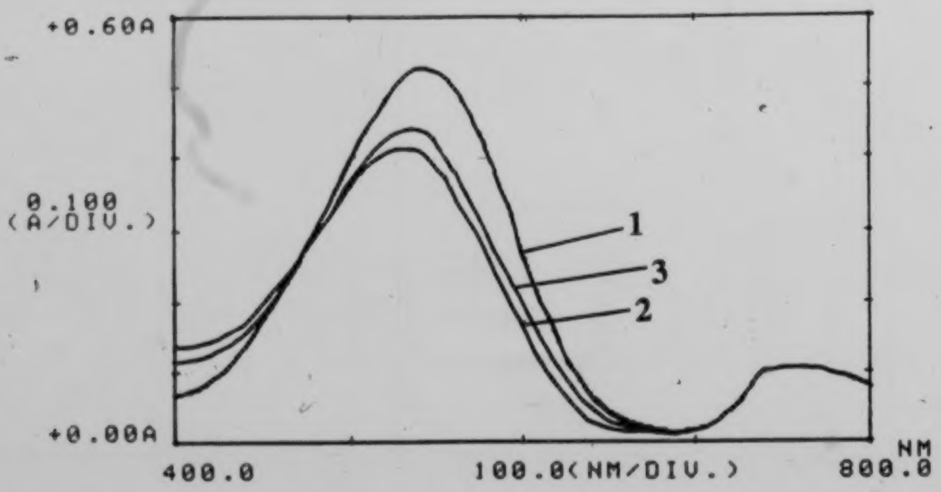
The blank solution containing ACVK only (spectrum 1) has a wavelength of maximum absorbance (λ_{max}) at 548 nm. However, after the addition of 0.3 mg/L of chlorine dioxide (spectrum 2) the absorbance at 548 nm decreases as the indicator undergoes oxidation and the observed λ_{max} for the oxidized complex appears at 532 nm (a hypsochromic shift). After two hours (spectrum 3) it can be seen that although the λ_{max} of the complex peak remains essentially unchanged, the absorbance of the peak has increased and in addition the peak appears to be slightly broader. Therefore it is possible that changes are occurring in the chlorine dioxide-indicator complex with time, although the exact nature of these changes cannot be determined at this time. However, the observed broadening of this peak explains the absorbance increases over time observed at 548 nm with this indicator. It should be pointed out, however, that these measurements were obtained using a 10-cm path length cell, the actual absorbance increases are relatively small and occur very gradually. Nonetheless, as previously stated, when using this reagent for chlorine dioxide determinations, the measurements should be made as quickly as possible to minimize any errors which may result from these effects.

2.5.12.3 Temperature Effects

A set of experiments were designed to evaluate the effect of sample temperature on the four colorimetric reagents studied in this work. The same solution compositions used for the timing experiments were chosen so that the effects of both parameters

Figure 2.8

Visible Spectra (from 400 to 800 nm) of Solutions Containing ACVK. All Spectra were recorded on a Shimadzu 160 Spectrophotometer Using a 10-cm Path Length Cell.



1. ACVK blank solution

2. ACVK solution immediately after the addition of 0.3 mg/L of ClO_2

3. ACVK solution containing 0.3 mg/L of ClO_2 after being allowed to stand for two hours in the spectrophotometer

could be evaluated on the same solutions. As before, experiments were carried out with both distilled (Millipore) and stilling basin water. The target sample temperatures were 5, 10, 15, 20, 25 and 30°C, with an uncertainty of ± 1°C being allowed for each temperature. Solutions were brought to the correct temperature either by placing in a refrigerator, or in a thermostatted water bath at 30°C. Intermediate temperatures were obtained by allowing solutions to either warm-up or cool down to the required temperature.

Procedure. All experiments were carried out in screw capped 250-ml dark glass bottles. Since duplicate solutions were prepared for each experiment twelve bottles were required for each experiment (two for each of the six temperatures). Blanks and samples were run separately, but on the same day and on the same sample water so that measurements of the change in absorbance would be comparable. The volumes of sample water pipetted into the blank and sample solutions were identical to those given in the time experiments described earlier. The bottles were then brought to the desired temperature. The colorimetric reagent and chlorine dioxide (where required) were then added and the absorbance (in triplicate) and the temperature of each solution was recorded. Plots of the average change in absorbance obtained for the duplicate analysis against solution temperature were then prepared. Graphs of the results obtained for each of the indicators are shown in Figures 2.9 and 2.10 and are discussed below;

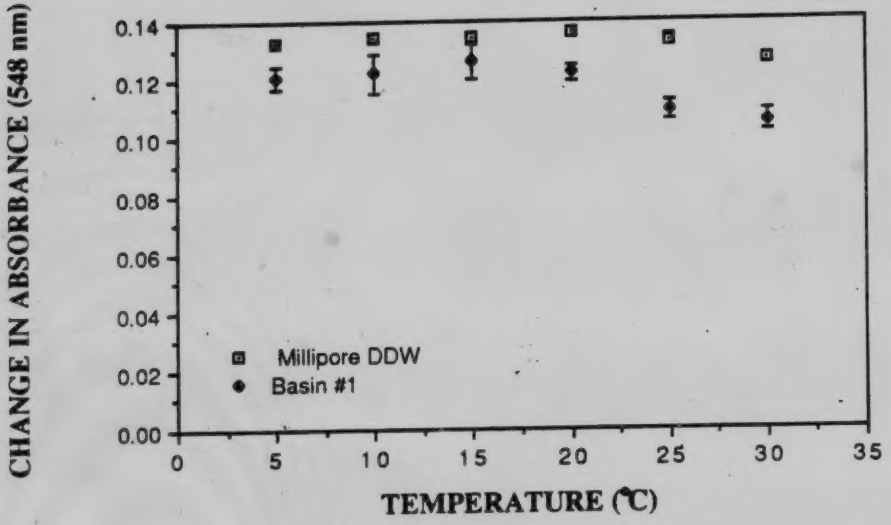
Results and discussion

(a) ACVK

From figure 2.9 a we can see that a similar trend is present for both distilled and stilling basin water samples. The change in absorbance remains relatively constant up to a temperature of about 20°C but then decreases with increasing temperature. This decrease is due to an increase in absorbance of the sample solutions at higher

Figure 2.9

(a) Plot of Change in Absorbance Against Temperature for Solutions Containing ACVK in Both Distilled (Millipore) and Stilling Basin Water.



(b) Plot of Change in Absorbance Against Temperature for Solutions Containing Amaranth in Both Distilled (Millipore) and Stilling Basin Water.

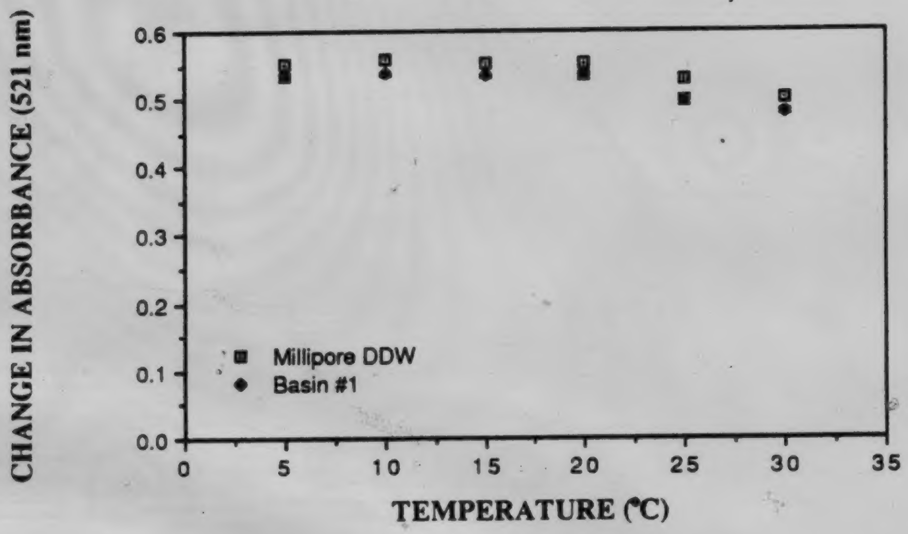
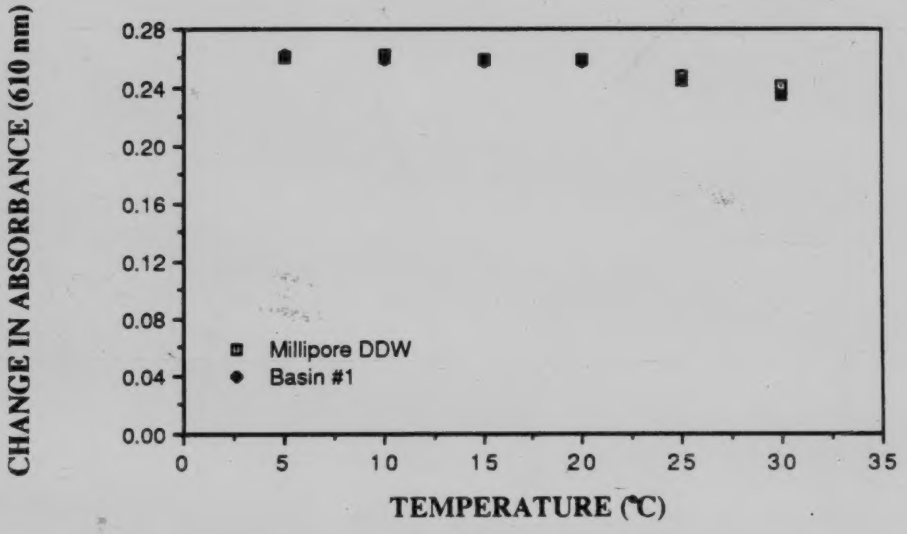
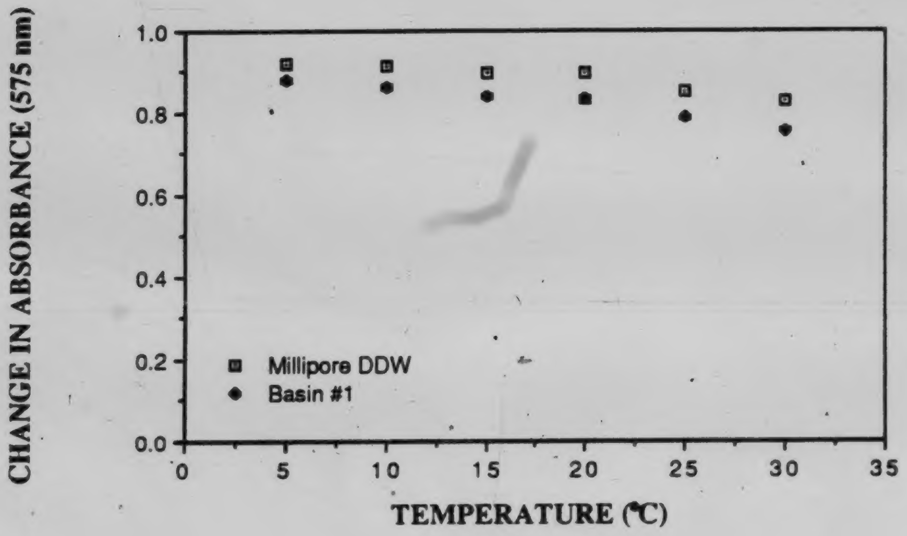


Figure 2.10

(a) Plot of Change in Absorbance Against Temperature for Solutions Containing Evans Blue in Both Distilled (Millipore) and Stilling Basin Water.



(b) Plot of Change in Absorbance Against Temperature for Solutions Containing Chlorophenol Red in Both Distilled (Millipore) and Stilling Basin Water.



temperatures and is most likely due to the thermal decomposition of a portion of the added chlorine dioxide prior to the addition of the colorimetric reagent. Since in these experiments the reagent is added immediately after the chlorine dioxide sample it appears that at temperatures much above 20°C chlorine dioxide rapidly decomposes. This has been previously reported[56]. The effect of increasing solution temperature on the absorbance of ACVK blank solutions in both types of water was minimal, indicating that the reagent itself is thermally stable over the range of temperatures studied in this work.

(b) Amaranth

Blank solutions containing only the sample water and the reagent showed a decrease in absorbance with increasing temperature, indicating some thermal decomposition of the reagent. However the extent of this decomposition is relatively slow. Absorbance readings for the blanks in distilled and basin water decreased by approximately 0.040, corresponding to approximately 2% of the total absorbance over the temperature range used in this work. The absorbance decreased more rapidly with increasing temperature. This trend was also observed to some extent in the samples up to a temperature of around 20°C. Above this temperature the effect of loss of chlorine dioxide is observed as it was for ACVK. A plot of the average change in absorbance with temperature is shown in Figure 2.9 b.

(c) Evans blue

For evans blue (see figure 2.10 a) a similar trend was observed at higher temperatures as was seen earlier in the plots of the average change in absorbance against temperature for the other two indicators. Below 20°C, however, the thermal stability of solutions of blanks and samples for both distilled and basin water with this indicator is excellent.

(d) Chlorophenol Red (CPR)

Chlorophenol red blank solutions in both distilled and basin water show a similar trend to those of amaranth in that the absorbance decreases with increasing temperature, indicating slow thermal decomposition of the reagent. Over the range of temperatures studied the decrease is approximately 4%. Sample absorbances are somewhat variable from 0 to 20°C although the general trend is toward decreasing absorbance. Above this temperature the absorbance decreases more rapidly, again because of chlorine dioxide decomposition. A plot of overall decrease in absorbance is shown in figure 2.10 b. As can be seen from the plot, this reagent is quite temperature sensitive. These results are in agreement with data obtained by Harp and Klein[71].

Although the information obtained from these experiments is somewhat limited, several conclusions can be drawn. Of the four indicators tested, all show good thermal stability over the range of temperatures studied, especially ACVK and evans blue. Chlorophenol red appears to be most sensitive to temperature variation in the samples. Since chlorine dioxide undergoes rapid thermal decomposition, samples held at or above 25°C for any length of time before the colorimetric reagents are added will show little or no chlorine dioxide present. An experiment in which 0.3 mg/L of chlorine dioxide was added to a sample of distilled water at 30°C and then allowed to stand for 15 minutes before the reagent was added showed that essentially no chlorine dioxide left after this time. Since the majority of treated water samples in Edmonton are in the range 0 to 20°C this should not be a problem. To obtain optimum results blank and sample solutions should be at approximately the same temperature; this is especially inmportant if the colorimetric reagent is CPR.

2.5.13 Comparison Studies

2.5.13.1 Initial Study

Having determined the limitations imposed on the various colorimetric reagents by turbidity, time, and temperature, the next goal was to design and carry out a series of experiments to compare the performance of the individual indicators for the analysis of low levels (less than 0.3 ppm) of chlorine dioxide in stilling basin water. These experiments were planned to parallel conditions for the analysis of "real" samples obtained downstream from the point of application of ClO_2 into the stilling basin. This would provide quantitative information on both the levels of ClO_2 in the basin and also on the detection limits of the various methods. The procedure for the initial series of these comparison experiments was as follows:

Procedure. Stilling basin samples were collected using the water sampler described previously from a depth of approximately 1.5 m below the surface at around the mid-point of stilling basin #1 at the Rossdale water treatment plant. Approximately ten samples were collected approximately 2 m from the basin outer wall and were composited and stored in a 20-L polyethylene container. This bulk sample was then stored at room temperature for 24 hours to allow sufficient time for the turbidity in the sample to settle out and also for any residual chlorine dioxide to decay. Aliquots of appropriate volume were then pipetted into the same 250-mL dark glass bottles as used in the previous experiments.

Since four colorimetric reagents were to be compared, and since only a limited number of solutions could be prepared and measured at a time, it was decided to test the reagents in pairs, for example evans blue and ACVK, and amaranth and CPR. This provided a series of six experiments in which each reagent was tested three times. For each experiment a four point standard calibration curve of change in absorbance against chlorine dioxide concentration over the range of 0 to 0.3 mg/L of chlorine dioxide was prepared for each indicator. In addition four spiked samples (together with suitable blanks) containing known amounts of chlorine dioxide were also prepared. For each sample the absorbance of each solution was measured in triplicate, the change in absorbance from the blank calculated, and the concentration determined from the calibration curve. This process was repeated for the second indicator of each pair using the same spiked samples. In this way the values obtained for the concentration of the samples could be directly compared. This procedure was repeated for each of the six experiments, with the spiked concentrations varying slightly from experiment to experiment. The results obtained are shown in Table 2.15.

Data analysis. Concentration values for the samples and the associated standard deviations were obtained statistically as follows. The method of least squares[27,28] was used to obtain the best fit line through the points for the calibration curve. The slope and intercept of the line were calculated using the statistics program Statworks (Datametrics Ltd). As a check the slope and intercept were also calculated manually in all cases using standard equations[103]. From values for the slope of the line (b) and the intercept (c) the concentration of chlorine dioxide in the unknown sample (x) could be determined using the relationship.

$$y = bx + c \quad (1)$$

where y is the average change in absorbance for the sample and all other quantities are as defined above. The standard deviation associated with the sample (S_{sample} or S_{unk}) was estimated from the measurements from which the straight line was obtained and the measurements made on the sample by the relation;

$$S_{sample} = s/b \left[(1/m + 1/n) + (y_{unk} - y)^2 / b^2 (\Sigma x^2 - (\Sigma x)^2 / n)\right]^{0.5} \quad (2)$$

Table 2.15

Comparison of Indicators for the Determination of Trace Chlorine Dioxide in Treated Water.

(1) Amaranth and Evans blue

		Amaranth		Evans blue	
Sample Number	ClO_2 added [1] (mg/L)	ClO_2 found (mg/L)	S_{sample} [2]	ClO_2 found (mg/L)	S_{sample} [2]
1	0.06	0.058	0.001	0.069	0.006
2	0.16	0.169	0.001	0.163	0.005
3	0.20	0.199	0.001	0.217	0.006
4	0.24	0.245	0.002	0.245	0.006

(2) Amaranth and CPR

		Amaranth		CPR	
Sample Number	ClO_2 added (mg/L)	ClO_2 found (mg/L)	S_{sample}	ClO_2 found (mg/L)	S_{sample}
1	0.08	0.082	0.006	0.085	0.009
2	0.16	0.160	0.005	0.164	0.008
3	0.20	0.211	0.006	0.199	0.008
4	0.24	0.241	0.006	0.235	0.009

(3) CPR and Evans blue

		CPR		Evans Blue	
Sample Number	ClO_2 added (mg/L)	ClO_2 found (mg/L)	S_{sample}	ClO_2 found (mg/L)	S_{sample}
1	0.06	0.058	0.004	0.062	0.007
2	0.12	0.124	0.004	0.121	0.006
3	0.16	0.169	0.004	0.157	0.006
4	0.20	0.199	0.005	0.210	0.007

[1] Concentration of ClO_2 added determined by UV measurement

[2] Standard deviations (S_{sample}) were calculated using equation (2) on page 164

Figure 2.15 (continued)

(4) Amaranth and ACVK

		Amaranth		ACVK	
Sample Number	ClO_2 added [1] (mg/L)	ClO_2 found (mg/L)	S_{sample} [2]	ClO_2 found (mg/L)	S_{sample} [2]
1	0.06	0.057	0.005	0.054	0.008
2	0.12	0.114	0.005	0.116	0.008
3	0.18	0.181	0.005	0.169	0.008
4	0.24	0.242	0.005	0.247	0.008

(5) Evans blue and ACVK

		Evans blue		ACVK	
Sample Number	ClO_2 added (mg/L)	ClO_2 found (mg/L)	S_{sample}	ClO_2 found (mg/L)	S_{sample}
1	0.06	0.061	0.010	0.053	0.011
2	0.12	0.130	0.009	0.114	0.011
3	0.18	0.188	0.009	0.164	0.010
4	0.24	0.238	0.010	0.234	0.010

(6) CPR and ACVK

		CPR		ACVK	
Sample Number	ClO_2 added (mg/L)	ClO_2 found (mg/L)	S_{sample}	ClO_2 found (mg/L)	S_{sample}
1	0.06	0.059	0.009	0.051	0.003
2	0.10	0.103	0.009	0.093	0.002
3	0.14	0.143	0.010	0.132	0.002
4	0.18	0.184	0.009	0.189	0.002

[1] Concentration of ClO_2 added determined by UV measurement

[2] Standard deviations (S_{sample}) were calculated using equation (2) on page 164

where m is the number of replicate measurements of the unknown, n is the number of points in the calibration curve (four in this case), y_{unk} is the average of the m replicates and Σ_x is the sum of the n measurements of the x values in the data set. The quantity s is given by the expression;

$$s = \left[1/(n-2)^{0.5}\right] \Sigma y^2 - (\Sigma y)^2/n - b^2 \left[\Sigma x^2 - (\Sigma x)^2/n\right]^{0.5} \quad (3)$$

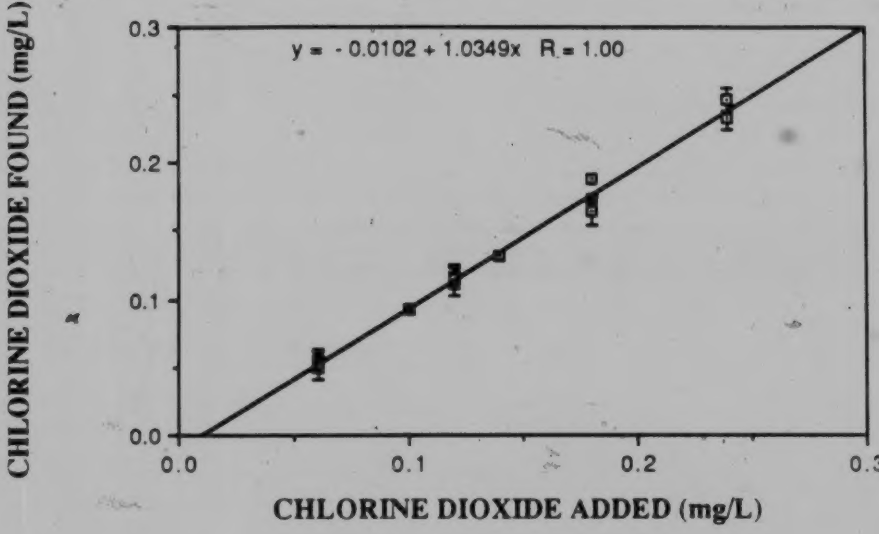
where Σy is the sum of the n measurements of the y values of the data set. A worked example for the calculations of the quantities s and S_{sample} (S_{unk}) can be found in reference 103.

Results. As can be seen from Table 2.15 and Figure 2.11 (which shows composite plots of the chlorine dioxide added against the chlorine dioxide found for each of the four reagents) the results obtained for the four indicators are generally satisfactory. The next step was to carry out a similar set of experiments at lower concentrations of chlorine dioxide. Preliminary experiments with ACVK indicated that below 0.03 ppm of ClO_2 the results obtained with this indicator were no longer reliable because absorbance changes were too small. Therefore this reagent was not studied further for trace levels.

To increase the sensitivity of the evans blue method the concentration of indicator was reduced and a longer path length cell employed. For example, if the amount of indicator was reduced by a factor of three, a 10-cm cell (as opposed to a 2-cm cell), could be used. The net result was an overall increase in sensitivity for the indicator by approximately a factor of five, making it comparable in sensitivity to CPR. This smaller amount of indicator was still, however, sufficient to maintain an excess of reagent relative to the amount of chlorine dioxide to ensure that all of the sample would

Figure 2.11

(a) Composite Plot of the Data Obtained for ClO_2 added against ClO_2 found for ACVK During the Reagent Comparison Studies (See Table 2.15).



(b) Composite Plot of the Data Obtained for ClO_2 added against ClO_2 found for Amaranth During the Reagent Comparison Studies (See Table 2.15).

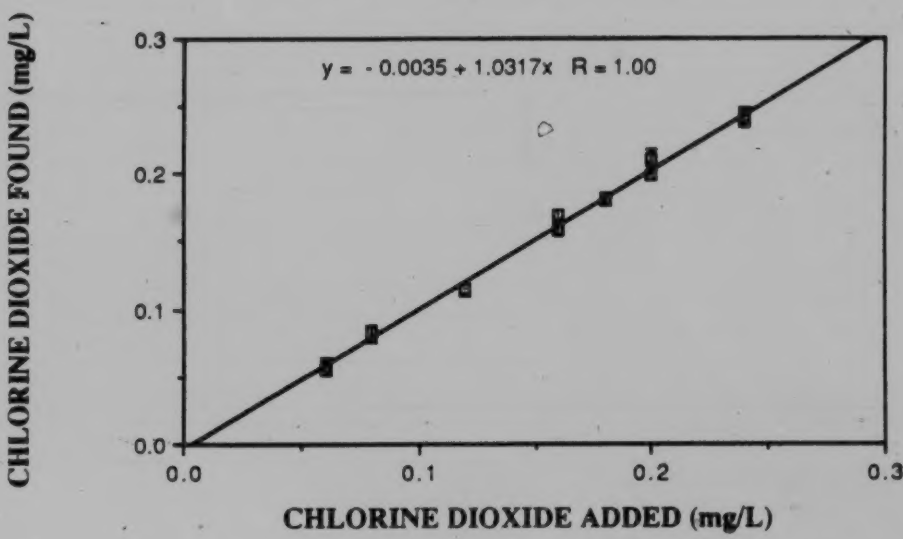
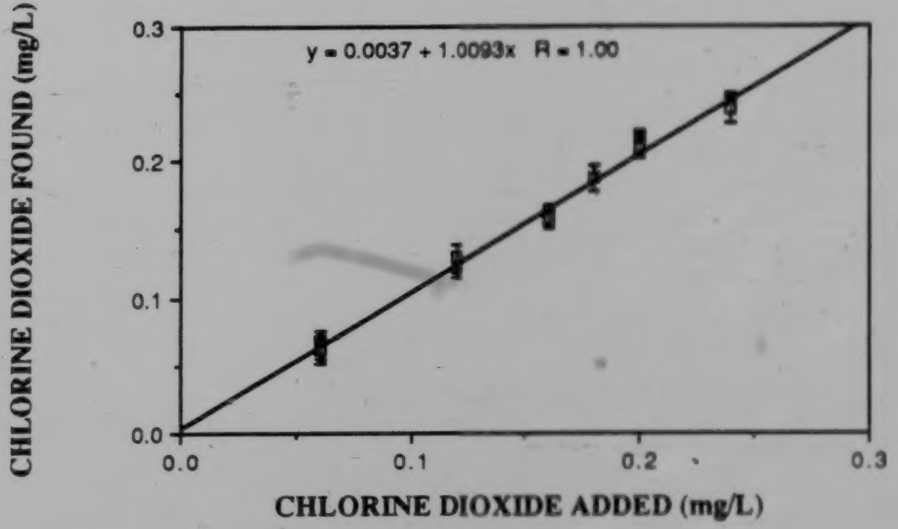
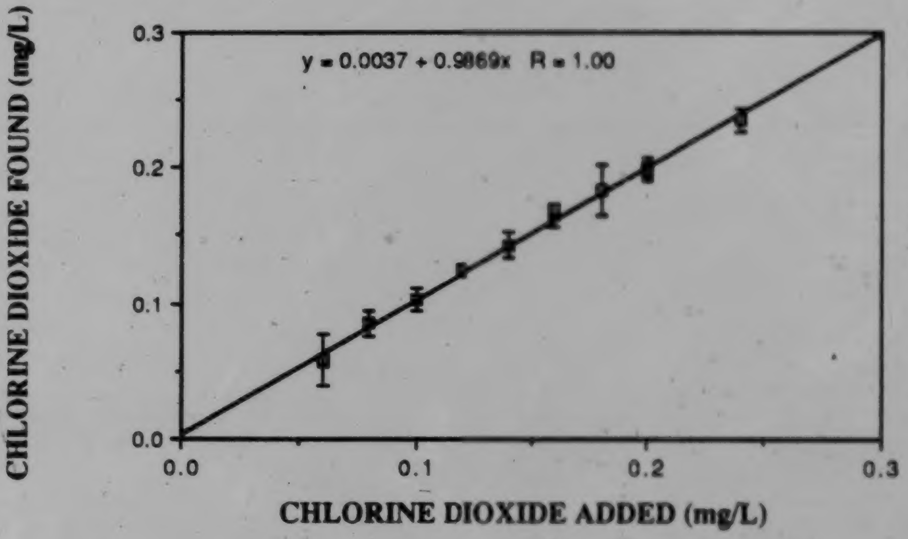


Figure 2.11 (continued)

(c) Composite Plot of the Data Obtained for ClO_2 added against ClO_2 found for Evans Blue During the Reagent Comparison Studies (See Table 2.15).



(d) Composite Plot of the Data Obtained for ClO_2 added against ClO_2 found for Chlorophenol Red During the Reagent Comparison Studies (See Table 2.15).



react. A calibration curve over the range 0 to 0.15 mg/L of ClO_2 under these conditions was found to be both linear and reproducible.

2.5.13.2 Low Level Study

Procedure. A set of measurements were carried out on low levels of chlorine dioxide using CPR, amaranth, and the modified evans blue procedure. The same conditions as described previously were used. Stilling basin samples were collected from approximately the same depth and location as in the preceding section and were allowed to stand for 24 hours prior to the experiment. For this experiment the amount of chlorine dioxide added to the samples was between 0.02 and 0.10 mg/L. The procedure for determination of the sample concentrations was analogous to that described earlier. The results obtained are shown in Table 2.16.

Results. The results were again very satisfactory, with excellent agreement being obtained for the three methods. At this point the last set of experiments which needed to be done was to determine the concentration of chlorine dioxide in "real" samples from the end of the stilling basin nearest the ClO_2 addition point.

2.5.13.3 Analysis of Real Samples

As mentioned previously, ClO_2 is generated "in situ" at the Rossdale water treatment plants. Once prepared it is piped to the stilling basins and added to the treated water, along with chlorine and fluoride, after the recarbonation step. All these chemicals are added via separate feed lines and are mixed by a mechanical mixer located at one end of the stilling basin. Dilution is rapid, and the ClO_2 reacts rapidly with organic and inorganic species present (generally in trace amounts) in the water.

A major problem was the choice of a sampling site to obtain a representative sample. The highest concentrations of chlorine dioxide occur nearest the point of application; however, due to the presence of the mechanical mixing device the water in this region is

Table 2.16

Low Level Comparison Study

		Amaranth		Evans Blue		CPR	
Sample No	ClO_2 added[1] (mg/L)	ClO_2 found (mg/L)	S_{sample}[2]	ClO_2 found (mg/L)	S_{sample}[2]	ClO_2 found (mg/L)	S_{sample}[2]
1	0.02	0.019	0.002	0.023	0.002	0.019	0.002
2	0.06	0.060	0.002	0.069	0.003	0.062	0.002
3	0.10	0.105	0.002	0.096	0.002	0.104	0.002

[1] Concentration of ClO_2 added determined by UV measurement

[2] Standard deviations (S_{sample}) were calculated using equation (2) on page 164

Analysis of Real Samples

		Amaranth		Evans Blue		CPR	
Site No[1]	Replicate	ClO_2 found (mg/L)	S_{sample}[2]	ClO_2 found (mg/L)	S_{sample}[2]	ClO_2 found (mg/L)	S_{sample}[2]
1	(a)	0.005	0.003	0.009	0.004	0.008	0.002
	(b)	0.007	0.003	0.006	0.004	0.008	0.003
2	(a)	0.028	0.003	0.029	0.004	0.022	0.003
	(b)	0.025	0.003	0.027	0.004	0.020	0.002

[1] The location of the sampling sites are shown in figure 2.12

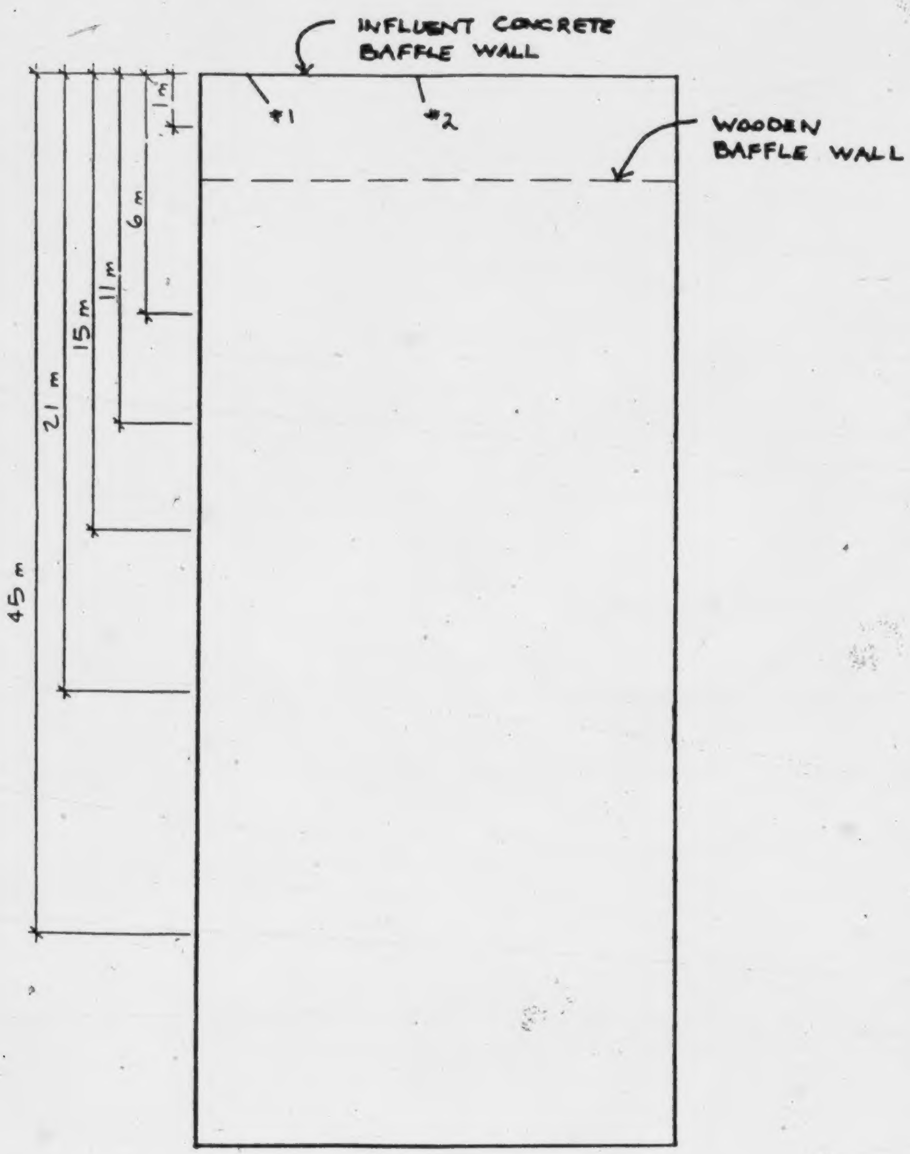
[2] Standard deviations (S_{sample}) were calculated using equation (2) on page 164

churned up and turbidities are extremely high. A good compromise appeared to be to collect samples from a position close to the concrete baffle wall which buffers the mixing zone from the bulk of the stilling basin (see figure 2.12). A second advantage to this location was that samples could easily be collected from a concrete walkway directly above the basin at that point. Collection was done using a device designed by members of the process development team (PDT) at the E.L.Smith treatment plant. This consisted of a metal rack containing two pockets into each of which could be placed a 250-ml dark glass bottle of the type used in the previous experiments. The bottles were lowered into the basin by ropes attached to a plastic holder. The bottles were closed with rubber stoppers which could be removed once the sampler was at the required depth by pulling on a separate line attached to each stopper. The filled bottles were then raised to the surface and the stoppers replaced. To prevent low results from decomposition of chlorine dioxide it was important that the colorimetric reagent (or reagents) be added as quickly as possible to the samples. From previous experiments we knew that the solution would be stable after the addition of the reagents but the problem of how to perform this operation as rapidly and efficiently as possible still remained. The following approach proved to be reasonably successful and was used in practice.

Procedure. The weights of the empty bottles were recorded and again after the addition of the water sample and reagents. Knowing the weight of the bottle and of the colorimetric reagents (determined separately) the weight, and hence the volume, of the sample water was calculated. A calibration mark was placed at 250 mL on each bottle. Preliminary experiments to determine the reproducibility of sample volumes obtained using these calibration marks indicated an uncertainty in volume of the order of ± 1% (2.5 mL) which was deemed acceptable for this work.

Figure 2.12

Plan View of Stilling Basin # 1 at the Rossdale Water Treatment Plant, Showing the Locations of the Two Sampling Sites Used to Collect Samples for the Real Sample Work. The Walkway From Which the Samples Were Collected is Located Directly Above the Influent Concrete Baffle Wall.


INFLUENT CONCRETE BAFFLE WALL
#1
#2
WOODEN BAFFLE WALL
1 m
6 m
11 m
15 m
21 m
45 m

In subsequent experiments all bottles used to collect the samples were weighed to the nearest mg (including the weight of the cap) and placed in a cooler. To collect a sample two bottles were transferred to the sampling device, stoppered, and lowered into the stilling basin to a depth of 2 m below the surface. The stoppers were removed and the bottles allowed to fill. The device was removed from the basin and a small quantity (50 mg) of sodium thiosulfate was added to one of the bottles to destroy the ClO_2 present and serve as the blank. Next, water was removed from each bottle with a pipet to bring the meniscus to the mark. The appropriate amount of the reagent solution was added to each bottle with a clean dry volumetric pipet. The bottles were closed with the screw capped tops, inverted several times to mix, and replaced in the cooler. The process was then repeated wirth a second pair of bottles to obtain a duplicate analysis. The bottles were returned to the lab, re-weighed (after drying the external surfaces of each bottle), the absorbance of each solution measured in triplicate, and the net change in absorbance recorded for each pair. The samples were analyzed as quickly as possible, and care was also taken to ensure that the bottles were maintained at approximately the same temperature. Since the variations in volume were small no attempt was made to correct the absorbance to take them into account.

Calibration plots were prepared as before, using water from a location close to the sampling locations. Several runs were carried out comparing the three reagents used for the low level work, CPR, amaranth and evans blue. The results of two of these runs, both carried out on the same day, are shown in Table 2.16. One set of samples was collected from a position approximately 1m from the basin wall (site #1) while the second set of samples was obtained from a position closer to the centre of the basin (site #2). Both sets were collected at a depth of 2 m below the surface. The locations of the sampling sites are shown on Figure 2.12.

Results. The results of these experiments (Table 2.16) indicate once again good agreement among the three reagents. In Table 2.16, the replicate determinations are designated as (a) and (b). As can be seen, concentrations of chlorine dioxide are relatively low at both of the the sampling sites. We conclude that the procedures using amaranth and evans blue developed during the course of this work can be successfully applied to the determination of low levels of chlorine dioxide in drinking water.

A discussion of the relative advantages and disvantages of each of the four indicators studied, based on the experimental data obtained, now follows.

2.6.1 Overall Summary for the Colorimetric Reagents (Advantages and Disadvantages)

(a) ACVK.

As mentioned previously, the two major advantages of the ACVK method are that only one reagent solution is required, and it can be used in the pH range normally encountered in water undergoing treatment with chlorine dioxide. It is also essentially interference free, and gives reproducible results on a day-to-day basis. Solutions of ACVK buffered at pH 9 to 10 are extremely stable and once prepared will last for up to a month when stored in a dark glass bottle at 4°C. Additionally, solutions of reagent treated water are relatively stable to variations in sample temperature.

On the other hand, ACVK has several drawbacks, the most serious of which is its inherent lack of sensitivity due to low absorbtivity. This limits its detection limit to around 0.03 mg/L of chlorine dioxide. Below this level, change in absorbance are too small for accurate measurements. Another disadvantage is that results in highly turbid samples (above 10 NTU) can be quite nonreproducible. However, for turbidities normally encountered in drinking water and in the stilling basin, which are normally in the range of 0 to 5 NTU, this is unlikely to be a major problem. Finally, as was observed during the ruggedness testing experiments, solutions of ACVK which come in contact with ClO_2 show a gradual increase in absorbance with time. At present the reasons for this change are not fully understood. For samples collected and stored for a period of time prior to analysis this could produce significant errors in the concentrations of chlorine dioxide determined. The extent to which this occurs seems to depend on the concentration of chlorine dioxide originally present in the sample.

(b) Amaranth.

Amaranth, one of the two compounds showing the most promise as a selective reagent for chlorine dioxide during the course of this work, has many of the advantages of ACVK. The procedure requires only a single reagent solution, can be used in the same pH range as drinking water and stilling basin samples, and buffered solutions of the reagent are very stable. This method has minimal interferences and is quite reproducible. The reaction with chlorine dioxide is rapid and irreversible. Amaranth is about four times more sensitive than ACVK owing to its higher absorbtivity; in addition, it is not as affected by sample turbidity as is ACVK.

There are few disadvantages to the use of amaranth as a spectrophotometric reagent for the determination of chlorine dioxide. It is less sensitive to chlorine dioxide than either CPR or evans blue, and copper (II) interferes at concentrations above 0.1 mg/L (100 ppb). The copper interference might be masked if necessary with EDTA or similar chelating agents.

(c) Evans blue.

Evans blue, the second reagent studied in this work, has similar advantages to amaranth and ACVK. Both iron (III) and aluminium interfere, but at levels seldom encountered in water being treated with chlorine dioxide in Edmonton. For example, Edmonton treats water obtained from the North Saskatchewan River with alum to remove suspended material by flocculation[4,5]. The solubility of hydrated aluminium oxide is so low at the pH used, however, that after softening and recarbonation the level is below the interference level of any of the reagents studied here. Because of its high absorbtivity, evans blue is comparable in sensitivity to CPR and calibration plots are linear to higher concentrations of chlorine dioxide than those with CPR. Solutions of evans blue are extremely stable with respect to time and temperature and measurements are essentially unaffected by sample turbidities as high as 5 NTU.

The reaction between ClO_2 and evans blue appears to be somewhat slower than for either amaranth and ACVK, but this is not a problem in the procedure outlined above.

(d) Chlorophenol Red (CPR).

The chlorophenol red method developed by Wheeler and co-workers[70] has as its main advantage high sensitivity owing to the high absorbtivity of the indicator. Other advantages include good reproducibility, stability of reagent solutions with respect to time, and relative insensitivity to sample turbidity. In addition the reaction between CPR and chlorine dioxide is rapid, and is complete within a few seconds of the addition of CPR reagent.

On the other hand, CPR has several drawbacks. One is that three reagents must be added in a specific order. This is inconvenient, especially in fieldwork. A second problem is that the optimum pH for the CPR-chlorine dioxide reaction is 5 to 5.5. This is not within the normal range of the majority of municipal drinking waters, and so a buffer is required to bring the sample into the correct pH range. Chlorophenol red also suffers interference from several species, including free chlorine (HOCl and OCl^-), and metal ions. Finally, the absorbance of solutions containing CPR-ClO_2 mixtures vary to some extent with temperature, requiring care that all solutions are at approximately the same temperature prior to analysis.

Of the indicators studied, either amaranth or evans blue is recommended, with amaranth our first choice on the basis of overall sensitivity, selectivity, and convenience. It is superior to the colorimetric reagents presently in use, and essentially free of interferences from other chlorine-containing species such as Cl_2, ClO_2^-, OCl^- and ClO_3^-. It is also little affected by metal ions at concentrations encountered in city of Edmonton drinking water, does not require pH adjustment, reacts rapidly, and is stable on storage as a reagent solution.

Because the procedures described here require a fair amount of experimental work, it was thought desirable to explore the possibility of automating the procedure. Therefore some preliminary flow injection analysis (FIA) studies using the indicators amaranth and evans blue were carried out with the aim of determining whether a method for the continuous analysis of water samples containing chlorine dioxide was feasible. The progress made towards that goal is outlined in the next chapter.

Chapter 3

Introduction

3.1.1 Definition of FIA and Components of an FIA System

Flow injection analysis (FIA) was initially pioneered by Ruzicka and Hansen[114] in 1974. Since that time it has become a useful and versatile analytical technique. The method is based on the injection of a liquid sample into a moving nonsegmented carrier stream of suitable liquid. The injected sample forms a zone which is transported towards a detector which continuously records absorbance, or another physical or chemical parameter (such as electrode potential), as a function of the passage of the sample material through a detector. The simplest flow injection system contains the following components:

(a) A pump to propel the carrier stream through the system.

(b) An injection port or valve to introduce a well defined volume of sample solution into the carrier stream in a reproducible manner.

(c) A reaction coil, generally of Teflon or stainless steel, in which the sample zone disperses and reacts with the components of the carrier stream.

(d) A flow-through cell or other detector system to monitor the signal corresponding to the concentration of the species being studied.

All the component parts are joined together with tubing (often Teflon) of internal diameters ranging from 0.3 to 1 mm. The signal from the detector, typically a peak, is related to the concentration of the analyte. Although peak height is most frequently used, it also possible to use peak width or area.

The time between sample injection and the occurrence of the peak maximum is termed the residence time (T_r). For a well designed FIA system the residence time is generally in the range of 5 to 20 seconds. Therefore two or three samples can be analyzed per minute. The injected sample volume (V_S) is typically between 1 and 200 μL, which means that the amount of reagents required per analysis can be kept low. Hence FIA can be described as a simple, automated, microchemical technique which is capable of having a high sampling rate with minimum consumption of sample and reagent.

From the preceding disscussion, we can see that FIA is based essentially on a combination of three principles: sample injection, controlled dispersion of the injected sample zone, and reproducible zone movement from the point of injection to the detector. In contrast with other methods of instrumental analysis, the chemical reactions take place while the sample is dispersing within the reagent, i.e while the concentration gradient of the sample zone is being formed by the diffusion process. The concept of controlled dispersion is very important in FIA, since reproducibility will be high only if the same processes occur for all samples injected.

FIA is a general solution-handling technique, applicable to a wide variety of measurements, from conductivity to enzymatic assays. The prerequisite for successful FIA assay is that the analyte be in a form in which it can be readily detected by the time it reaches the detector. Also, sufficient time must be allowed for the production of the compound to be detected as the sample mixes with the reagents in the system. It should be noted, however, that neither homogeneous mixing nor production of a "steady state" are required for a successful analysis. This is one of the major advantages of this technique.

3.1.2 A Review of the Effect of Standard FIA Parameters on the Dispersion of the Sample Zone

The following is a brief review of the most important variables involved in the design of a flow system in terms of dispersion coefficient, residence time and other flow parameters.

When designing a FIA system it is important to know how much the original sample solution is diluted on its way to the detector and how much time has elapsed between sample injection and readout. For this purpose the diffusion coefficient (D) has been defined[114] as the ratio of concentration of sample material before and after the dispersion process has taken place. The relevant equation is;

$$D = C^{\circ} / C \quad (1)$$

where C° is the original concentration of the injected sample solution. If the analytical readout is based on the measurement of the peak height then this equation becomes;

$$Ds^{max} = Cs^{\circ} / Cs^{max} \quad (2)$$

where Cs^{max} is the concentration corresponding to the maximum of the recorded signal (peak height).

Generally speaking, whatever the readout signal used, a value of D = 2 means that the sample solution has been diluted in a ratio of 1 : 1 with the carrier stream. Thus, knowledge of D and T_r adequately describes the concentration ratios in an FIA system and allows comparisons of both the sample/reagent dilutions and reaction conditions between conventional and FIA procedures. Sample dispersion can be defined either as limited (D = 1 to 3), medium (D = 3 to 10) and large (D >10). Systems employing all these dispersion regions have been used for many analytical tasks.

The simplest way of measuring the dispersion coefficient when using a spectrophotometric detector is to inject a known volume of a dye solution into a colorless carrier and monitor the absorbance of the dispersed dye zone. To obtain the value of Ds^{max} the height of the recorded peak is measured and compared with the distance between the baseline and the signal obtained when the cell has been filled with undiluted dye. Provided the Beer-Lambert law is obeyed, the ratio of respective absorbances gives a Ds^{max} value that describes the FIA manifold, detector and detection system. Changing the configuration of the system will of course change the value of the diffusion coefficient. The influence of various parameters on the dispersion will now be discussed.

The first of these is the influence of the sample volume. It has been shown experimentally[115] that changing the injected sample volume is a powerful way to change the dispersion of the system. An observed increase in the peak height (and thus in sensitivity of measurement) is achieved by increasing the volume of the sample injected. Conversly, dilution of overly concentrated material is best achieved by reducing the injected volumes.

The geometry of the system between the injection port and the detector has a profound influence on the dispersion of the system. The influence of both the length of the reactor coil (L) and internal diameter (d) of the tubing have been extensively studied[115,116]. The use of small diameter tubing will result in lower $S_{1/2}$ values ($S_{1/2}$ is defined as the volume of sample solution necessary to reach 50% of steady state value, which corresponds to the condition where $D = 2$) and hence lower dispersion because the same amount of sample will occupy a longer length of tube (Θ) according to the equation;

$$S_v = \pi\,(0.5\,d)^2\Theta \quad (3)$$

where S_v is the volume of sample injected into the system (in µL), and d is the internal diameter of the tubing (in mm). Thus the sample will have restricted contact with the carrier stream, and will therefore be less easily mixed and dispersed. Hence from equation (3) we can see that if the tube diameter is halved, the sample will occupy a fourfold-longer portion of the tube. If a limited dispersion system is required, the system should be constructed with the shortest possible piece of narrow bore tubing between the injection port and the detector.

Even if a medium dispersion FIA system is required, it is more economical to use narrow bore tubing. Both sample and reagent economy improve, which may be a saving if quantities of sample or reagent are limited. Also, for the same flow rate the pumping rate (Q) in a tube of diameter d is only one quarter of that required for tubing of diameter 2d. On the other hand, practical considerations prevent the use of tubing of too-narrow a bore. There are three reasons for this.

Firstly, resistance to flow will increase, which prevents the use of a low pressure (such as a peristaltic) pump. Secondly, the system can easily be blocked by solid particles. This makes the use of these systems inpractical for the assay of certain materials, unless the samples are filtered beforehand. Finally, the flow cell of the most frequently used detector, the spectrophotometric detector, must have an optical path with an inside diameter of at least 0.5 mm. Otherwise sufficient light will not pass through. The use of narrow tubing will cause undesired nonuniformities in the flow pattern in the detection area.

To sum-up, the optimum internal diameter of tubing in most FIA systems is of the order of 0.5 mm. However, 0.7 mm internal diameter tubing can be used for systems which require high dispersion, and 0.3 mm internal diameter tubing can be used when a limited dispersion system is required.

The mean residence time, T_r (av), of an FIA system having uniform internal diameter tubing depends on the tube length (L), the tube diameter (d), and the pumping rate (Q) according to the equation;

$$T_r\,(av) = \pi\,(d/2)^2\,L/Q = L/F \qquad (4)$$

where F is the linear flow velocity. Thus, when designing a medium dispersion system where the sample has to be mixed and made to react with the components of the carrier stream, the natural tendency is to increase L in order to increase the mean residence time T_r (av). However, the dispersion of the sample zone will also increase as L increases. This "bandbroadening" effect will result in a loss of sensitivity with a corresponding lowering of the sampling rate. It has been shown[115,117]that dispersion increases with the square root of the mean residence time (or the distance travelled, L). Hence, we can see that although longer mean residence times can be obtained by increasing the length of the tube, it is simply not worthwhile above a certain limit. As an alternative to increasing L, one can instead decrease the pumping rate and keep the tube length as short as is practical. Because of the physical distances between all the individual components of the FIA system, it is necessary to make certain compromises. In practice the length of a typical FIA manifold is between 10 and 100 cm (for tubing of internal diameter of 0.5 mm). Residence times of up to 20 s can easily be obtained by judicious selection of the flow rate. Longer residence times may also be obtained by intermittent pumping, in which for part of the cycle the forward movement of the carrier stream is stopped[118].

The geometry of the FIA microreactor has also received considerable attention. Several configurations have been used in FIA systems. These include straight and coiled tube geometries (both commonly used) as well as more esoteric designs such as the single bead string reactor (SBSR) and the knitted reactor in which the coils of the tubing are actually knotted. Another alternative is a modified mixing chamber design which incorporates a small chamber where the components are rapidly mixed before passing to the detector. The main function of these reactors is to increase the intensity of radial mixing and thereby reduce the parabolic velocity profile that normally forms in the axial direction when a sample solution is injected into a laminar flow carrier stream. As a result, the reagent becomes more readily mixed with the sample, and also axial dispersion of the sample zone is reduced.

Relaxation of the laminar profile in the radial direction is best achieved by creating local turbulence, which in practice can be done by changing the direction of flow. Elements of fluid which are close to the tube walls and hence are slower moving are moved closer to the centre. Elements closer to the centre are conversely shuffled closer to the wall. The more frequently this process is repeated the more symmetrical will be the concentration gradient within the sample zone, and hence the more symmetrical will be the peak shape.

In straight tube configurations the parabolic profile is relatively undisturbed; as a result the observed peak shape is asymmetrical.

For the coiled tube geometry, secondary flow within the coil promotes mixing in the radial direction, and as a result more symmetrical and narrower peaks are generally produced than with the straight tube configuration. The tighter the coil the more pronounced this effect is likely to be[119]. However, a symmetrical peak will only be observed if L is relatively long (greater than 1 m), and since a typical FIA coil is considerably shorter than this, a typical FIA peak in a coiled reactor will be asymmetrical.

The characteristics of other geometries, which are less common, will not be discussed here. Only straight tube and coiled reactors were utilized in this work.

3.1.3 Kinetics of FIA

The majority of FIA methods are based on the use of chemical reactions. The product (or products) of these reactions are measured by a detector. FIA is useful in this respect because it can accommodate a wide variety of chemical systems. In most cases, FIA peak size and shape is the result of two processes: physical dispersion, and chemical reactions occurring in the sample zone. These two processes occur essentially simultaneously. However, in FIA mutual interaction of these processes is complex because the dispersed zones are not homogeneous. Therefore an exact description of the chemical kinetics taking place in FIA systems is difficult. A detailed review of kinetics in FIA is beyond the scope of this thesis, but a number of papers have been published on the subject[120-123] and the reader is referred to these articles if further information is required.

Generally speaking, for an FIA system to be successful it is necessary that the reaction be relatively fast. A very slow reaction is unlikely to be useful in FIA because very long residence times would be required and the sensitivity of such a system would be correspondingly low. However, differences in rates of certain reactions occurring in the same chemical system can be used to discriminate between various analytes and increase sensitivity. This technique of kinetic discrimination has found a number of applications; an example applied to the analysis of chlorine dioxide is illustrated in the next section.

3.2.1 Applications of FIA to the Analysis of Chlorine Dioxide

Several FIA systems which have been constructed for the analysis of chlorine dioxide (see chapter 2) are briefly reviewed here.

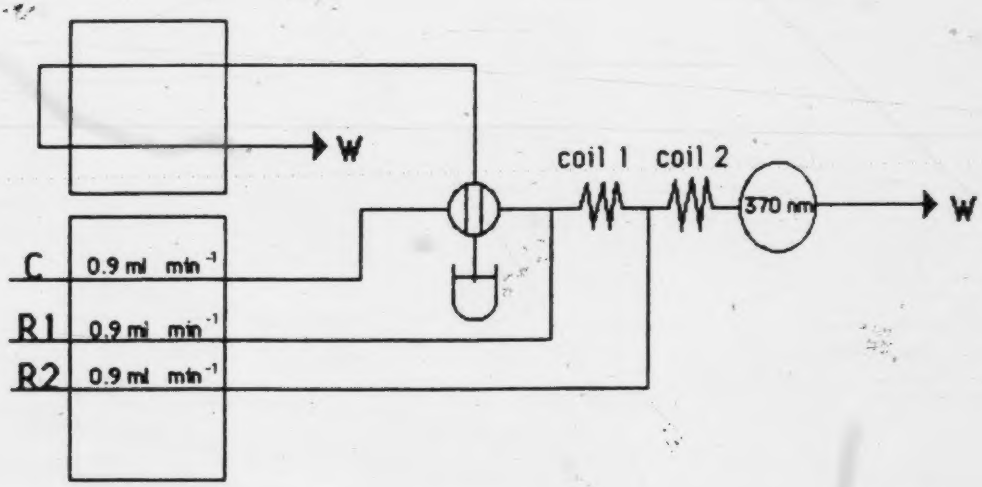
Gordon and co-workers developed a gas diffusion FIA system[81] in which additional selectivity is achieved by the use of a porous Teflon membrane (0.45μm pore size), which allows only gaseous species to pass. A detection limit of 0.25 mg/L of chlorine dioxide has been achieved with this system. Spectrophotometric detection at 359 nm is used.

A chemiluminescence detection system for FIA has been reported by Saksa and Smart[78]. This system was applied to the analysis of chlorine dioxide in various sample waters and has a reported detection limit of 0.20 mg/L. Another FIA system utilizing chemiluminescent detection has been reported by Hollowell and co-workers[79]; the chemiluminescent reagent used was luminol. These authors have also reported FIA systems for the measurement of ozone, chlorate, and other disinfectant species[82,124]. A recent paper by the same group[82] describes an ingenious FIA system for the analysis of several chlorinated species, including chlorine dioxide,.based on the concept of kinetic discrimination mentioned earlier. A schematic of the manifold for this system is shown in figure 3.1. The method is based on the fact that several chlorine species react with potassium iodide at various pH values to produce iodine[66,125,126]. The absorbance due to I_3^- is measured at 370 nm with a standard 1-cm path length flow cell. Discrimination is achieved by varying the reaction conditions, and hence the rates, of the reactions taking place. As described earlier in the section on the Aieta method in chapter 2, pH influences the equilibria of reactions between chlorine species and iodide.

Another way to achieve additional selectivity is by the use of suitable "masking agents". If two species react under the same conditions, then one of them can often be effectively removed from the solution by addition of a suitable masking agent. This selective reaction with one species enables the concentration of the other to be determined. For example, oxalic acid may be added to a system if it is desired to determine chlorine dioxide in the presence of chlorine at a range of pH from 7 to 8.5. Oxalic acid reacts rapidly with chlorine to form carbon dioxide. Oxalic acid reacts only

Figure 3.1

Schematic Diagram of the FIA Manifold Used by Gordon and Co-Workers to Determine Various Disinfectant Species (Reproduced from Reference 82).


W
coil 1
coil 2
370 nm
W
C
0.9 ml min⁻¹
R1
0.9 ml min⁻¹
R2
0.9 ml min⁻¹

C; Carrier Stream of Triply Distilled Water
R1; 0.02 or 12 M HCl
R2; 0.3 M KI

very slowly with chlorine dioxide and hence allows its determination without significant interference from chlorine. A detection limit of 0.3 mg/L of chlorine dioxide has been reported for this system.

Experimental Work

3.3.1 Objectives

The initial objectives in this FIA study were to design and build a system to determine chlorine dioxide reproducibly and simply using spectrophotometric detection. We also hoped to devise a system for possible use in the field. The indicators amaranth and evans blue that were developed during the course of this project were chosen as the spectrophotometric reagents to be studied. The reasons for their choice were as follows:

Since one of the objectives was to keep the design of the system as simple as possible, only methods requiring one reagent were considered. In this way only a single line would be required to provide the carrier reagent, and samples could be introduced into the flow of carrier by means of a standard injection valve. The chlorophenol red (CPR) method requires that three reagents be added in a specified sequence, and although it is possible to design a FIA system to accomodate this, the system would be more complex. Therefore we did not consider CPR further. The other reagent studied earlier, ACVK, was by a considerable margin the least sensitive of the three indicators. Therefore we decided to concentrate on amaranth and evans blue for these studies.

As mentioned in the introduction, it is not necessary to achieve either quantitative reaction between reagent and sample or to approach steady state conditions for an FIA analysis to be successful. The reaction between chlorine dioxide and both amaranth and evans blue is reasonably fast, however, and so these potential problems in their use are minimized.

3.3.2 Construction and Components of the Trial System

With this in mind the components for a trial FIA system were assembled. The decision was taken to aim for a system of medium to high dispersion if possible. Since a wide variety of components were not readily available it was necessary to make some compromises in equipment. The trial system consisted of the following.

The pump was a Gilson miniplus 2 peristaltic pump. This is a small, low pressure peristaltic pump designed to produce only very small "pulses" in operation. This is an advantage because pulsing can be a major problem in FIA work.

The sample injection valve was a 10 µL capacity 2-way slider valve (Laboratory Data Control). The valve has two positions. In one position sample is injected into the flow of carrier; in the other sample may be drawn into the valve while it is isolated from the flow of carrier.

The delay coil (microreactor) was either a coil or a straight tube length of 0.8 mm I.D Teflon tubing (Mandel, Rockwood Ont.) of various lengths.

The flow cell was a 1-cm Hellma flow through compact cell (30 µL volume) with suprasil windows. The inlet and outlet were two 210-mm lengths of Teflon tubing (1.0 mm I.D), both single flanged and fitted with a washer and short screw thread fitting. The flow cell was connected to the rest of the system with standard fittings.

The detector was a HP 8451 diode array spectrophotometer (Hewlett Packard). This instrument is a single beam, microprocessor-controlled, UV-visible, high speed spectrophotometer . Absorbance spectra over a range in wavelength from 190 to 820 nm can be obtained in 0.1 seconds with a 0.7 second repetition rate. The spectrophotometer operating system is controlled by an HP-85A personal computer which includes a built in CRT and combined printer/plotter. The data can also be displayed on an external plotter. A diagram of the experimental setup is shown in Figure 3.2.

3.3.3 Calibration of Pump Tubing

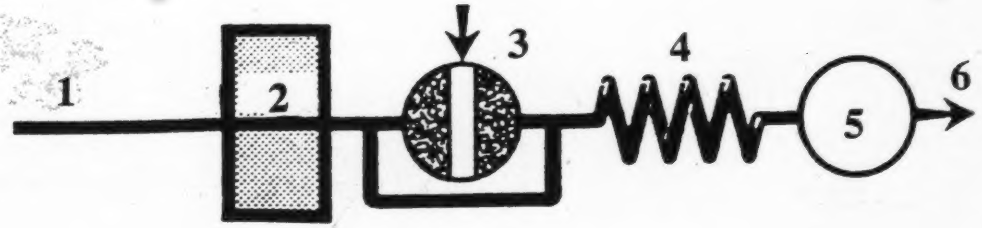
Procedure. For a peristaltic pump such as the Gilson minipuls 2 used in this work the range of flow rates that can be obtained depends largely on the bore of the pump tubing. A further degree of control may be obtained by varying the pump rotor speed settings. Various sizes of pump tubing can be obtained that provide a variety of flow rates. In this work the pump tubing (Technicon Corporation, Tarrytown, NY) was designed to give a flow rate of 1.25 mL/min. To install the pump tubing the rotor collar on the pump was released and the tubing then wrapped around the rotor. The tubing was locked into place by fastening the tubing stops securely into position. A Teflon female luer adaptor (Valco Instruments Co Inc, Houston, TX) was then inserted into each end of the tubing. To prevent the possibility of leaks the connections were secured by short loops of copper wire. Standard Teflon box connectors were used to join the pump tubing to the other system components. These connectors were used throughout to join the various lengths of Teflon.

We first determined the range of flow rates which could be obtained with the pump tubing at pump settings between 100 and 999. These settings represent a percentage of the total capacity of the pump. For example, a setting of 100 indicates that the pump is operating at 10% of its maximum rotor speed. The setting of 999 provides the maximum flow rate obtainable for a particular diameter of pump tubing. If higher rates of flow are required larger diameter pump tubing must be installed.

To ensure there was no blockage or other impediment to flow, distilled water was initially pumped for five minutes at a pump setting of 500 (50% capacity). The pump

Figure 3.2

Schematic Diagram of the Single Line FIA Manifold used for the Initial Experiments.



System Components

1. Carrier Reagent (Amaranth)
2. Gilson 2 Minipuls Peristaltic Pump equipped with nominally 1.25 mL/minute pump tubing (Technicon)
3. Fixed volume (10 µL) 2-way Slider Sample Injection Valve (Laboratory Data Control)
4. Delay coil, Various Lengths of 0.8 mm ID Teflon Tubing (Mandel)
5. Flow Through Cell (Hellma, 30 µL Volume) and HP (Hewlett Packard) 8451 Diode Array Spectrophotometer Detector
6. To Waste

was then reset to a value of 100 and, after another five minutes to allow the flow rate to reach a steady value, the flow of water from the pump was diverted into a clean, dry 50-ml flask (which had been previously weighed to the nearest 0.1 mg). After exactly fifteen minutes the flask and its contents were re-weighed and the volume of water collected during the fifteen minute time period determined. In this way the flow rate at a given pump setting can be calculated in mL/min. The process was repeated for a number of different settings; the results are shown in Figure 3.3.

3.3.4 Setting the Experimental Parameters

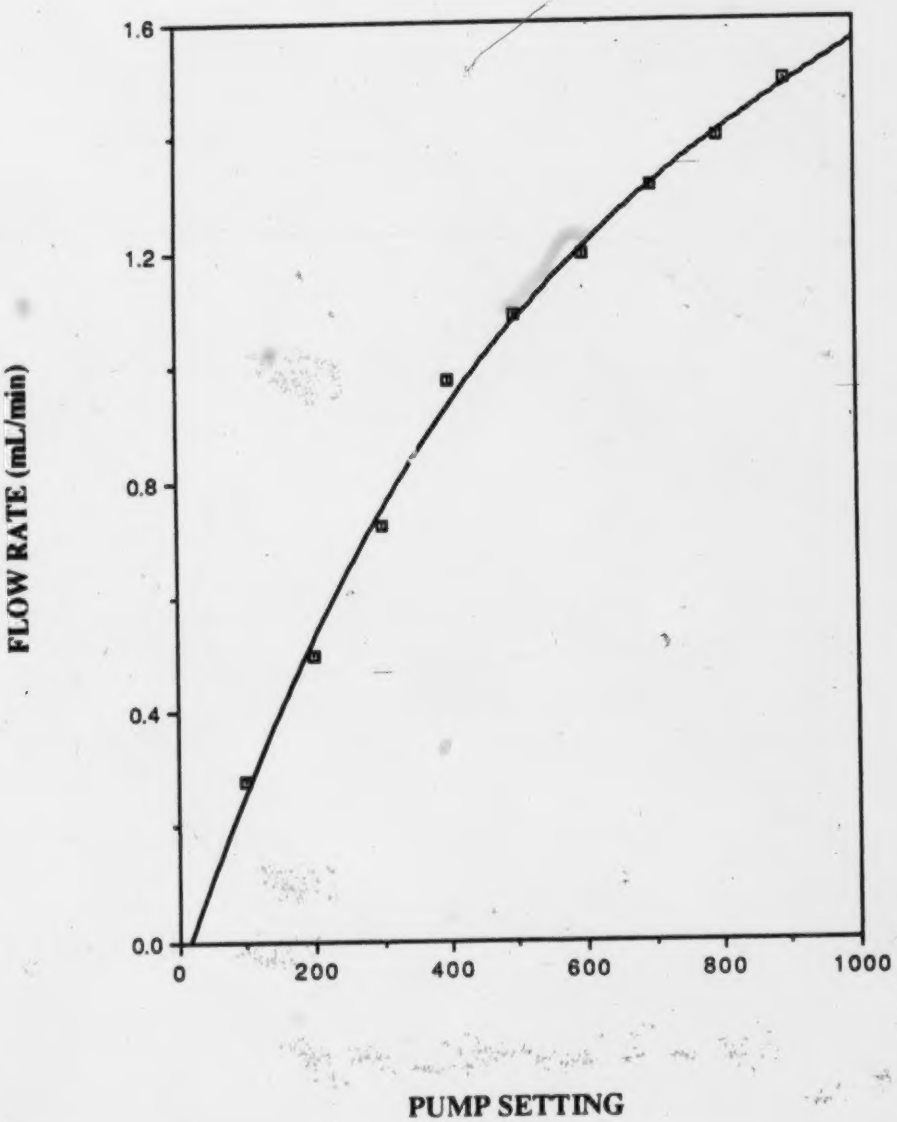
Before the FIA experiment was run the experimental parameters to be used in the experiment were defined using the HP 8451A. One of the major advantages of this instrument is that it can be independently programmed. This is especially useful if one wishes to make a series of repetitive measurements with a well defined timing sequence. Once the spectrophotometer had warmed up, the following sequence of instructions was entered using both the keyboard (model HP 89057A) attached to the instrument and the controls on the panel of the spectrophotometer itself.

The Y-scale appropriate to the experiment was initially entered, followed by the appropriate wavelength for the reagent (520 nm for amaranth and 610 nm for evans blue). The HP 8451A has a bandwith of 2 nm, with a photodiode centered at each even numbered wavelength value from 190 to 820 nm (316 diodes in total). Although odd-numbered values are accepted by the processor, they are automatically changed to the next lower even-numbered wavelength before being used.

Having set the Y-scale and the wavelength, the next set of parameters to consider were the time settings. The 8451A allows the operator to set four time parameters, which together define the experiment. A series of consecutive runs with an identical timing sequence can then be done. The four parameters which can be set are:

Figure 3.3

Calibration Plot of Observed Flow Rate (in mL/minute) Against Pump Setting for Pump Tubing (Nominally 1.25 mL/minute) Used in This Work.



(a) Integration time (I), which is time over which the instrument will integrate the signal before processing the data.

(b) Repeat time (R), the time at which a repeat measurement of the absorbance (or transmittance) of the sample will be taken by the instrument.

(c) Start time (S), the time at which the instrument will begin to take measurements after the "EXECUTE" command is given. This allows introduction of a time delay if required.

(d) End time (E), the time at which the instrument will stop taking measurements after the "EXECUTE" command is given.

These time inputs are preceded by the "MEASURE" command (obtained by pressing the appropriate button on the control panel) and must be entered in the sequence given. As an example, if we wished the instrument to take a measurement on the samples every five seconds, with a 1 second integration time, starting immediately after the "EXECUTE" is given and ending sixty seconds later, the appropriate command sequence would be:

```
MEASURE 1, 5, 0, 60 EXECUTE
```

An example of one complete program for experiments using amaranth as the carrier reagent is:

```
05 Y SCALE 0 to 0.2 EXECUTE.
10 LAMBDA 520 EXECUTE.
20 MEASURE 0.2, 5, 0, 60 EXECUTE.
30 END EXECUTE.
```

Note that the "EXECUTE" command must be given after every line in the program. The number associated with each line on the left hand side is the program line number.

The program is initiated by the command sequence "RUN PROGRAM" followed by "EXECUTE".

3.3.5 The FIA Experiment (General Procedure)

Procedure. Once the experimental parameters had been set and the system fully assembled (see Figure 3.2), distilled water was pumped through the system for five minutes at a flow rate of approximately 1 mL/min. The function of the distilled water is to provide a zero absorbance reference for the spectrophotometer and to stabilize the pump system. Once the flow rate appeared steady the command "REFERENCE" followed by "EXECUTE" was given to the instrument by pressing the appropriate buttons on the panel. After allowing water to flow through the system for a further two minutes, the above instructions were repeated.

Once the zero had been set the reservoir of water was then replaced by reagent solution, either amaranth or evans blue. Stock solutions (nominally 2 x 10^{-4} M) of each reagent were prepared as described earlier. To prepare reagent solutions for these FIA experiments a 10-mL aliquot of the appropriate stock solution was pipetted into 250 mL of chilled distilled water in a 250-mL volumetric flask, and the contents mixed by inversion. The reagent solution was then pumped through at a flow rate of approximately 1 mL/ min for five minutes before being adjusted to the desired flow rate for that particular experiment. After allowing the reagent to flow through the system for a further five minutes the program written earlier for the experiment was initiated by pressing "RUN PROGRAM" followed by "EXECUTE" on the instrument control panel. The output on the CRT screen was a straight line corresponding to the maximum absorbance of the reagent solution. A hard copy of the data for the individual measurements for each run can be printed out on the instrument printer if required by the command sequence "PRINTER, EXECUTE".

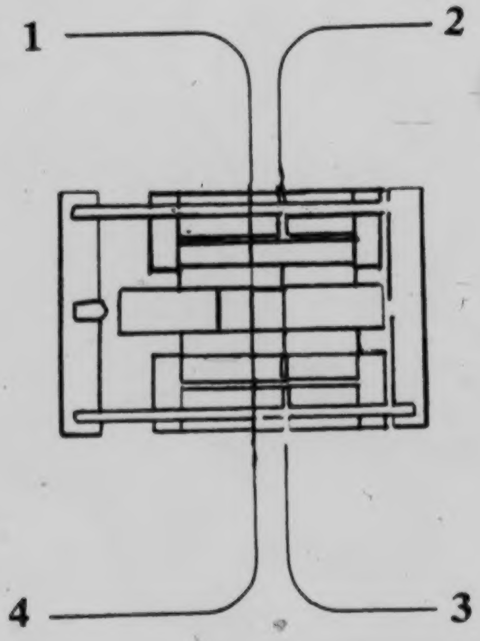
Before injecting the chlorine dioxide standards, several runs were carried out with distilled water, which acts as the blank in the experiment. The injection valve was then flushed several times with distilled water. Sample solutions (either distilled water or chlorine dioxide) were drawn into the valve from the sample reservoir by a syringe assembly. This assembly consisted of a stainless steel syringe needle connected to one port of the injection valve by a short length of Teflon tubing and connector. A schematic of the injection valve and syringe assembly is shown in Figure 3.4. After flushing the valve with sample, a 10-µL portion was injected into the carrier stream. Immediately after each sample was injected the data collection program was initiated as described earlier. Upon completion of each run (the spectrophotometer automatically stops taking readings after a time period specified by the program) the injection valve slider bar was pushed back to its initial position to isolate the valve from the flow of reagent carrier, another sample was loaded into the valve, and the above sequence repeated. Three replicate injections were made of all solutions.

Chlorine dioxide standards were prepared in distilled water by dilution of a stock solution prepared by the Masschelein procedure described in chapter 2. Standards were made up in 50-mL volumetric flasks and were freshly prepared for each experiment. Preliminary experiments were carried out to determine the appropriate volumes required for each standard. These were standardized by the UV method described earlier. The absorbance of the standards was recorded in triplicate at 360 nm using a 1-cm cell on the HP 8451 A spectrophotometer.

For each experiment, six chlorine dioxide standards were run in addition to distilled water. Three replicate injections were made for all solutions. Between standards the injection valve was flushed several times with the new solution to minimize cross contamination. At the end of each experiment the valve and the lines were flushed with

Figure 3.4

Schematic Diagram of the Two-Way Slider Valve used in the Initial Work.



1. To Syringe (Sample Introduction)
2. To Peristaltic Pump
3. To Delay Coil and Detector
4. To Sample Reservoir

distilled water for fifteen minutes. After this time the pump was switched off and the flow cell was removed from the cell holder of the spectrophotometer.

The procedure outlined above was used for all the FIA experiments carried out in this work. The various experiments performed, together with the results obtained, are discussed in the next section.

3.3.6 Experiments with Amaranth as the Carrier Reagent

Initial experiments were carried out using amaranth as the carrier reagent. It was decided that to start with we would use a combination of a relatively low flow rate of reagent and a long delay coil. Under these conditions the sample zone will experience considerable dispersion and the residence time of the sample will be long. It was hoped that this experiment would provide some indication of the feasibility or otherwise of using amaranth as a colorimetric reagent for chlorine dioxide by FIA.

The initial experimental parameters were as follows:

Length of Delay Coil = 136.3 cm (0.8 mm ID)

Flow Rate = 0.98 mL/min

The sample volume was by necessity constant at 10 μL, the fixed capacity of the injection valve. The preset program parameters were:

Y-Scale = 0 to 0.2 Absorbance units

λ_{max} = 520 nm

Integration Time = 0.2 s

Repeat Time = 5 s

Start Time = 0 s

End Time = 60 s

For subsequent experiments with amaranth the Y-scale, wavelength and start time were kept constant at the values indicated.

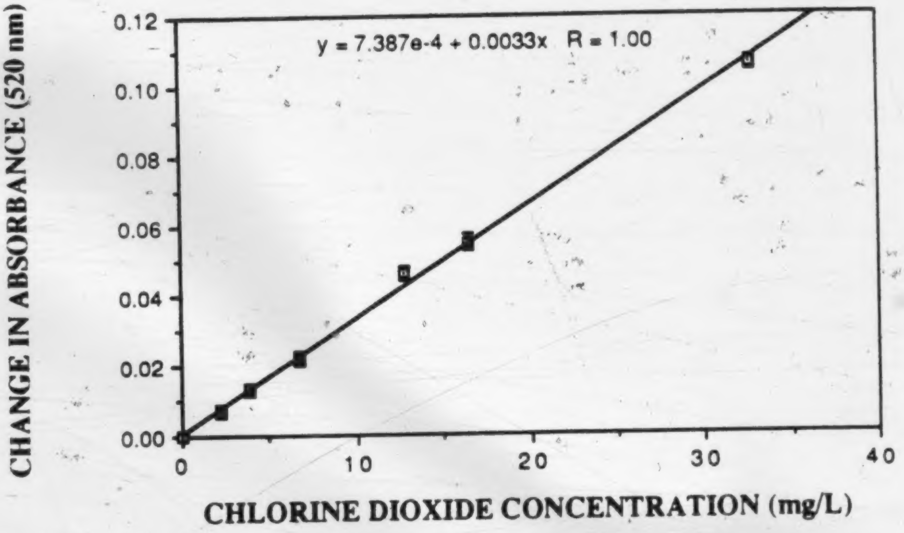
Results. The results of this preliminary experiment were encouraging. A linear calibration curve was obtained over a range of chlorine dioxide standards up to 33 mg/L. A plot of the change in absorbance against chlorine dioxide concentration is shown in Figure 3.5 a. To obtain this plot the average absorbance obtained for each of the standards was subtracted from that of the distilled water blank as was done previously. The overall standard deviation associated with each point was calculated from the individual standard deviations associated with the standard and the blank by the equation given earlier. Reproducibility between runs for the same standard was very good. A plot of absorbance against time from injection (in seconds) for one of the runs for each of the standards and distilled water is shown in Figure 3.5 b. From the figure we can see that the residence times (the elapsed time between the time of the sample injection and the time at which the peak minimum occurs) under these conditions are of the order of 30 to 35 seconds. To check reproducibility several runs were carried out under the same conditions as the previous experiment. It was found that the calibration curves were reproducible on a day to day basis.

3.3.6.1 Effect of Flow Rate on Sample Zone Dispersion

To determine the effect of flow rate, several replicate runs were made at different flow rates on a chlorine dioxide standard of approximately 33 mg/L. For the various flow rates the values of the repeat time (R) and end time (E) were varied as necessary. The start time (S) and the integration time (I) were kept constant at 0 and 0.2 seconds respectively. All other parameters were as given earlier. Figure 3.6 shows the results for one run at each flow rate used in the experiment. From the figure we can see that as the flow rate increases, the residence times decrease because the sample zone is carried

Figure 3.5

(a) Plot of Change in Absorbance Against Chlorine Dioxide Concentration for 136.3 cm Delay Coil using Amaranth as Carrier Reagent.



(b) Plot of Observed Absorbance Against Time for One Run Each of Chlorine Dioxide Standards and Distilled Water with the 136.3 cm Delay Coil.

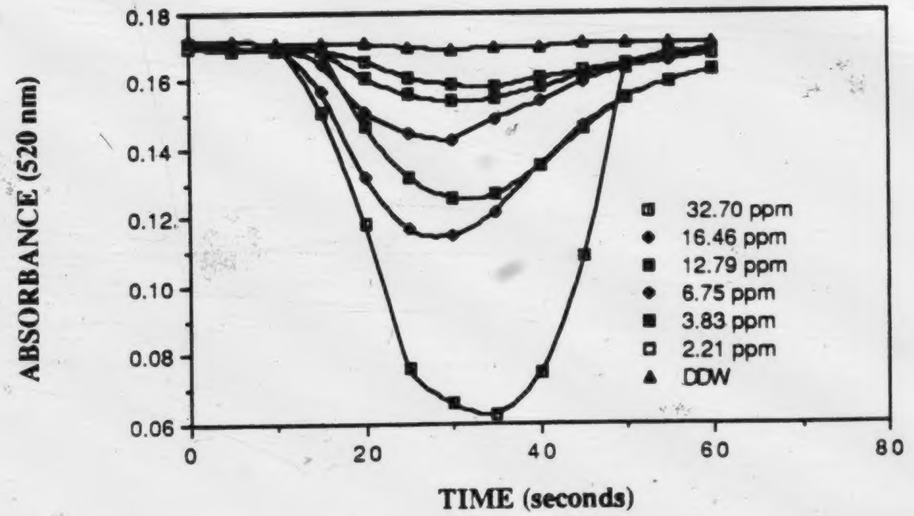
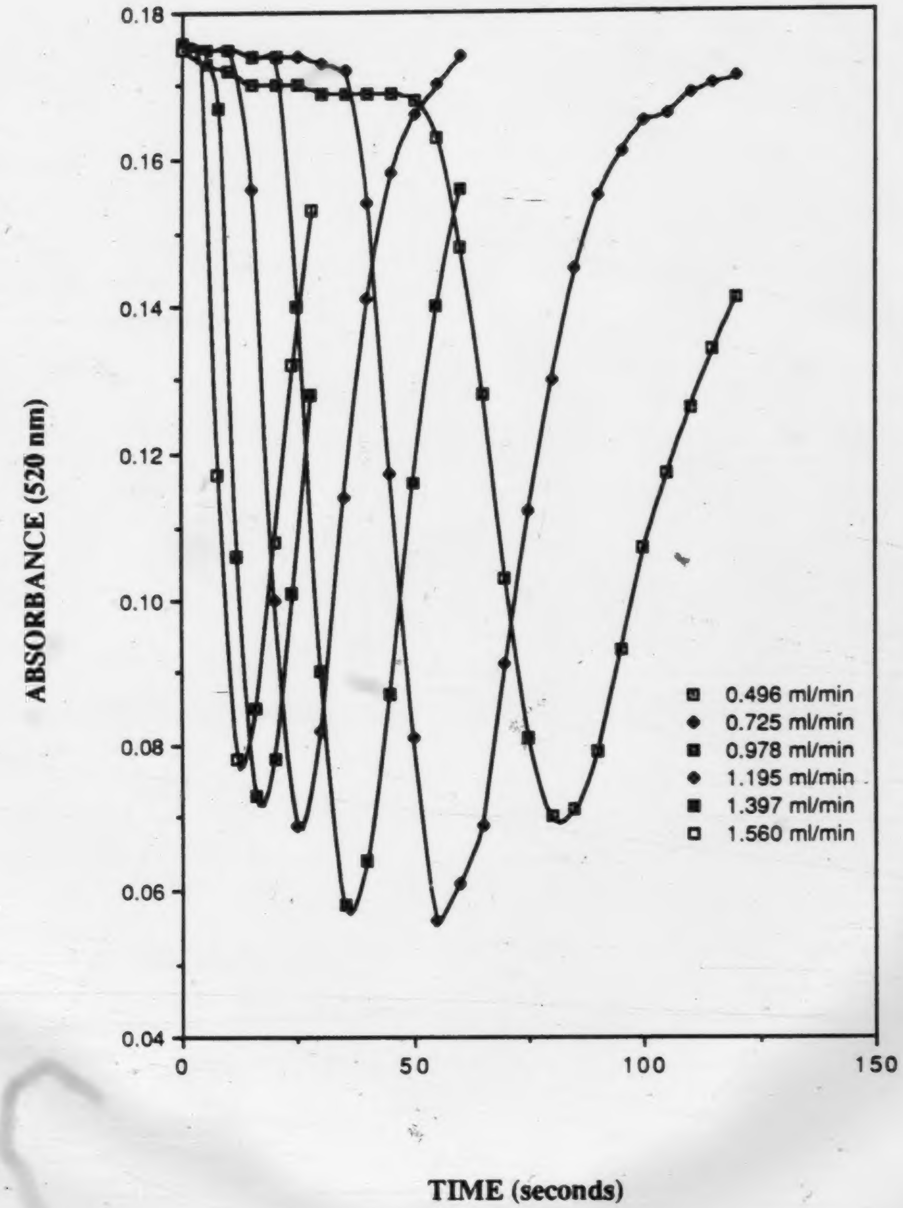


Figure 3.6

Effect of Flow Rate on Residence Time and Peak Height for an Approximately 33 mg/L Standard of Chlorine Dioxide in FIA using Amaranth as Carrier Reagent (Length of Delay Coil = 136.3 cm).



through the system at a faster rate. However, shorter residence times mean that the sample has less time to react with the reagent, which may decrease sensitivity. In FIA it is important to strike a balance between these factors. While it it obviously desirable to achieve the greatest sensitivity possible, use of lower flow rates results in a decrease in the efficiency of the system because the number of samples which can be processed in a specified time is reduced. From the figure we can see that the optimum compromise occurs at a flow rate of about 0.98 mL/min. At this flow rate the absorbance change is near maximum and the residence time of approximately 30 seconds is relatively short. By coincidence this was the flow rate initially chosen for these experiments.

3.3.6.2 Effect of Decreasing the Length of the Delay Coil

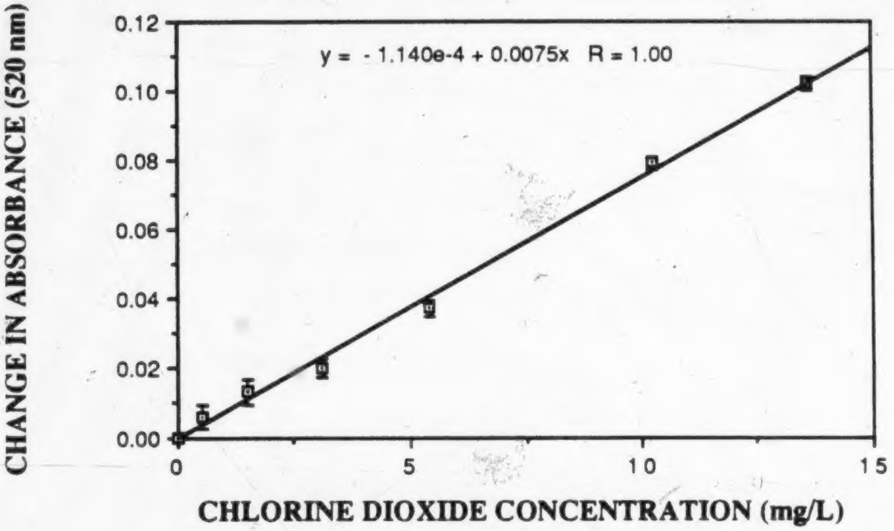
Although the results obtained in these preliminary experiments were promising the ClO_2 level was relatively high. We were interested in obtaining data at lower levels of chlorine dioxide, between 0 and 1 mg/L. To achieve greater sensitivity it was necessary to reduce the dispersion of the system, and hence the residence time. This can be done by either increasing the sample volume or decreasing the length of the delay coil. The former was not possible because the capacity of the available sample injection valve was fixed at 10 μL. Therefore a number of experiments were carried out using delay coils of various lengths (all with an internal diameter of 0.8 mm). These were prepared as required from lengths of teflon tubing. The ends were flared and appropriate fittings attached to allow the coil to be joined to the rest of the FIA system. An experiment was also carried out with no delay coil present, but the peaks produced with this configuration were distorted and reproducibility was poor. The optimum length of the delay coil was found to be 17.5 cm, and the optimum configuration straight rather than coiled. Calibration curves of change in absorbance against chlorine dioxide concentration were linear and reproducible over a range of chlorine dioxide standards from 0 to 15 mg/L, when using amaranth as the carrier reagent. An example of a calibration curve is shown in Figure 3.7 a. The standard deviation associated with each point was obtained as described previously The experimental parameters for these runs were:

Length of Delay Coil = 17.5 cm (0.8 mm ID)
Flow Rate = 0.98 mL/min
Repeat Time = 1 s
End Time = 50 s

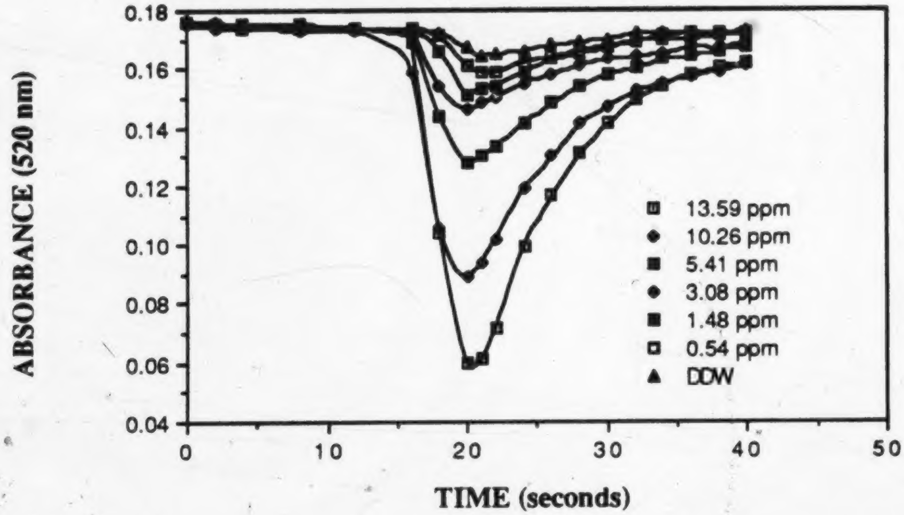
All other parameters were the same as for the initial experiments. The optimum flow rate was determined experimentally to be 0.98 mL/min. A plot of absorbance against time for one run for distilled water and one for each of the standards is shown in Figure 3.7 b. From the figure we can see that the observed residence times are considerably shorter than before, of the order of 19 to 22 s. The dispersion (D) for this configuration was measured as described earlier, by injections of dye with distilled water as the carrier. The average (peak) absorbance of the sample reaching the detector was compared to that obtained for the reagent as the carrier. The dispersion, calculated by dividing the latter quantity by the former, was found to be of the order of 19 ± 3 for amaranth. Thus this system may be classified as a high dispersion system (see introduction), with the sample zone being dispersed not only in the delay coil but also in the tubing associated with the flow cell.

Figure 3.7

(a) Plot of Change in Absorbance Against Chlorine Dioxide Concentration for an FIA System using a 17.5 cm Delay Coil and Amaranth as Reagent.



(b) Plot of Observed Absorbance Against Time from Injection for One Run of Each of the Chlorine Dioxide Standards and Distilled Water with a 17.5 cm Delay Coil.



3.3.7 Experiments Using Evans Blue as the Carrier Reagent

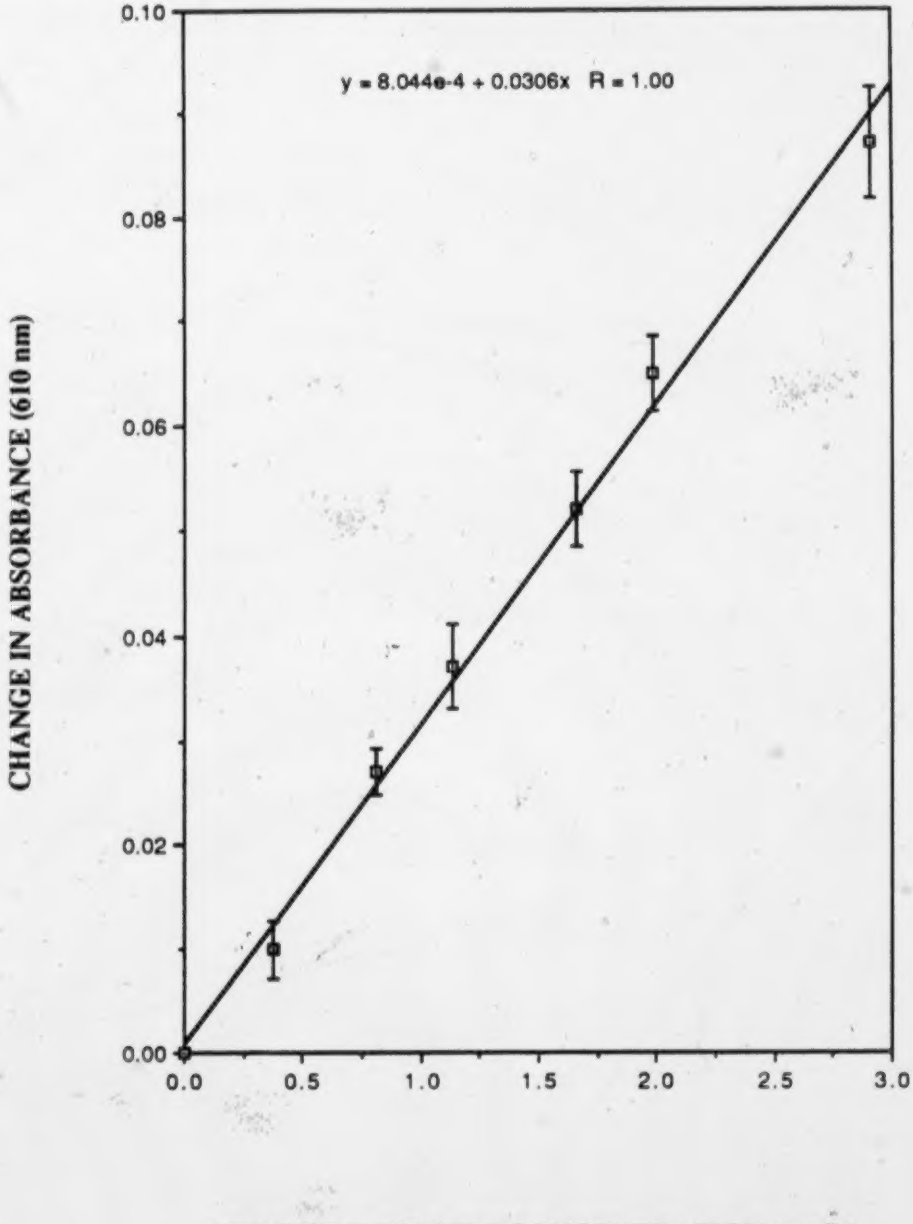
Overall, the results obtained to this point were promising, and it seemed feasible to increase the sensitivity of the system further either by use of a more sensitive reagent or by use of a larger volume of sample. We therefore evaluated the properties of evans blue as the carrier reagent. Since evans blue has a considerably higher absorbtivity than amaranth it was expected to be more sensitive. A set of experiments were carried out for evans blue under the conditions found to be the optimum for amaranth so that direct comparison could be made between the two indicators. Evans blue was found to indeed be more sensitive under the same conditions, by approximately a factor of four. Calibration curves plotted for chlorine dioxide standards over the range of 0 to 4 mg/L were found to be linear and reproducible. An example of one of several curves is shown in Figure 3.8. For this figure the experimental and program parameters were as follows;

λ Max = 610 nm
Y-Scale = 0.to 0.7 Absorbance
Length of Delay Coil = 17.5 cm
Flow Rate = 0.98 mL/min
Integration Time = 0.2 s
Repeat Time = 1 s
Start Time = 0 s
End Time = 50 s

The observed residence times for the samples and the dispersion measured for evans blue were similar to that obtained previously for amaranth. Attempts to increase the sensitivity by changing the length of the delay coil were not successful and these conditions appeared to represent the optimum with the current system.

Figure 3.8

Plot of Change in Absorbance Against Chlorine Dioxide Concentration For 17.5 cm Delay Coil Using Evans Blue as Carrier Reagent.



3.3.8 Effect of Increasing the Sample Volume

The major limitation to increased sensitivity appeared to be the fixed volume capacity of the injection valve. Injecting larger volumes of sample solution is an excellent way to increase sensitivity (see introduction to this chapter). Therefore we considered other types of valves in which the injection volume could be varied. One such type is a rotary injection valve with a number of injection ports (typically four to eight) that can be used in a variety of configurations. Rotary valves are widely used in FIA systems.

Although a number of different designs of rotary valves are commercially available the basic function is the same. The valve has two positions: sampling and injection. In the sampling (or load) position sample is drawn into the valve (either manually or more usually by a syringe) to fill an external sampling loop of a known volume. The reagent is isolated from the loop and is diverted into a by-pass loop to avoid a buildup of back-pressure in the valve while the loop is being filled. Once the loop is full the valve is then rapidly switched to the inject position by rotating the rotor through a fixed angle (either 60 or 90°, depending on the valve) and left there until the sample is completely swept out of the loop by the flow of reagent. Depending on the design of the valve the sample volume may be changed either by changing the loop itself, or by adding an additional length of Teflon tubing to the existing loop.

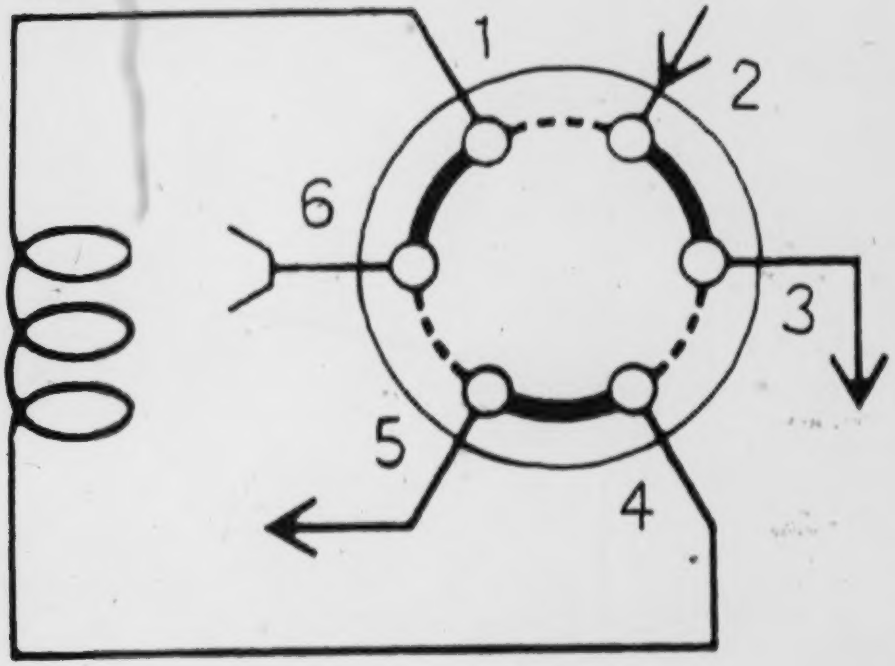
For this work the rotary valve used was a Rheodyne (Rheodyne Inc, Cotati, Cal) type 50, Teflon, 4-way valve. This is a six port valve equipped with 0.8 mm i.d tubing. The volume of the external loop, approximately 70 µL, fixed the minimum sample volume that could be injected. In this valve the sampling loop is not interchangeable, but the size of the loop can be increased by adding a length of tubing as described above. A schematic diagram showing the connections and the valve configuration in the load and inject positions is given in Figure 3.9.

Procedure. Experiments were carried out at the optimum conditions established earlier for amaranth and evans blue. The only difference from the previous system was the addition of the Rheodyne rotary valve in place of the fixed capacity slider valve. Standard calibration curves of the change in absorbance against chlorine dioxide concentration were plotted for amaranth and evans blue over a range of chlorine dioxide standards from 0.2 to 1 mg/L. Examples of calibration curves obtained for each indicator over this range are shown in Figure 3.10.

Results. For amaranth the calibration curves were linear over the range 0.2 to 0.8 mg/L of chlorine dioxide and showed good reproducibility on a day to day basis. For evans blue the curves were linear over a more limited range of concentration of chlorine dioxide, from 0 to 0.6 mg/L. However, the reproducibility of the calibration curves was only moderate. This suggested that under these conditions steady state was being approached for this indicator. Measurement of the dispersion coefficient of the system as described earlier gave a value for D of 3 ± 0.6, which indicated that the system in this configuration now had low dispersion. It appeared from the above results that it might be possible to increase the sensitivity for the amaranth reagent still further by increasing the sample volume yet again. Therefore an additional piece (10 cm) of 0.8-mm ID tubing was added to the sampling loop to produce a loop of approximately 120 μL capacity. However, although calibration curves could be obtained over approximately the same range of chlorine dioxide standards as above, i.e from 0 to 0.6 mg/L, no significant increase in sensitivity was observed. In addition considerable problems were encountered with the formation of air bubbles in the sampling loop.

Figure 3.9

Schematic Diagram of Rheodyne Rotary Injection Valve Showing Connections and Configuration in Sampling (Load) and Injection (dashed line) Positions.

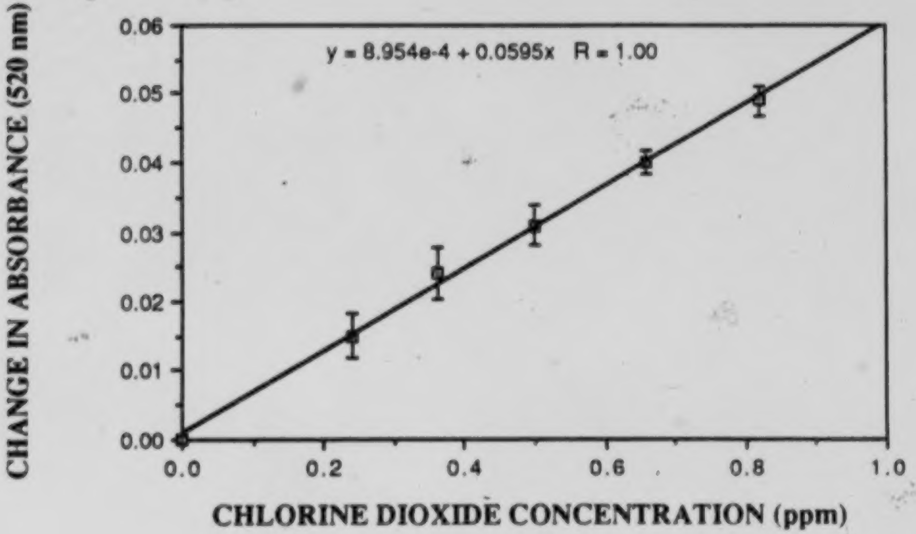


Ports 1 and 4; connected together to form the external sampling loop (70 µL)
Port 2; to peristaltic pump
Port 3; to detector via delay coil
Port 5; to sample reservoir
Port 6; to syringe assembly (sample introduction) and waste

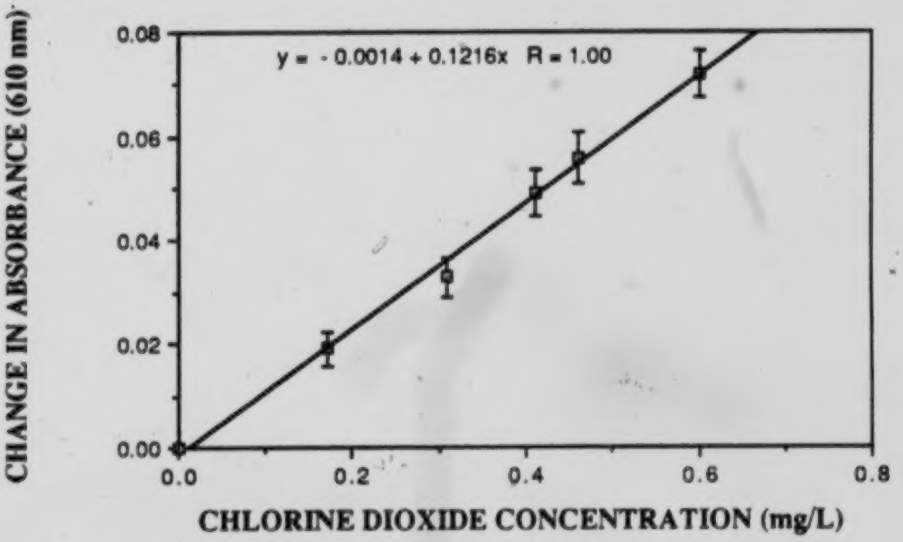
The solid black lines show the valve switching pattern in the Load position
The dashed lines show the valve switching pattern in the Inject position

Figure 3.10

(a) Calibration Curve of the Change in Absorbance Against Chlorine Dioxide Concentration (70 µL Sample Volume) using Amaranth as Carrier Reagent.



(b) Calibration Curve of Change in Absorbance Against Chlorine Dioxide Concentration (70 µL Sample Volume) using Evans Blue as Carrier Reagent.



Therefore it appears that a 70-μL sample injection volume is the optimum for the amaranth reagent under these conditions.

Although the results obtained to date were certainly encouraging, all the experiments previously described were carried out in distilled water. Therefore as a final experiment the chlorine dioxide concentrations of several spiked samples were determined in treated (tap) water.

3.3.9 Determination of Chlorine Dioxide in Tap Water

Procedure. In this experiment a standard calibration curve was plotted as described previously over a range of chlorine dioxide standards from 0 to 0.6 mg/L using amaranth as the carrier reagent. Then two spiked samples containing a known concentration of chlorine dioxide (determined by UV) were prepared in sample water in 50-mL volumetric flasks and the absorbance due to the samples was determined by injecting 70 μL aliquots of the sample (via the Rheodyne rotary valve) into the carrier stream. A blank solution of sample water was also run to enable values of the change in absorbance to be determined for the samples. Three replicate injections were made for all samples and standards to ensure rerproducible results were obtained. Questionable data points were repeated as necessary by making up a fresh solution of the desired concentration of chlorine dioxide and re-running the solution on the FIA system. The experimental parameters for this experiment were as follows:

Water Source = Treated Tap Water
λ Max = 520 nm
Y-Scale = 0.to 0.2 Absorbance
Injection Volume = 70 μL
Length of Delay Coil = 17.5 cm
Flow Rate = 0.98 mL/min

Integration Time = 0.2 s

Repeat Time = 1 s

Start Time = 0 s

End Time = 30 s

The concentrations of the samples and the associated standard deviations (S_{sample}) were obtained statistically as described previously in chapter 2 of this thesis in the section dealing with the comparison studies of the colorimetric reagents. The slopes and intercepts of all calibration curves were obtained both from the Statworks (Datametrics Ltd) computer program and manually by the use of standard equations[103]. A number of runs were carried out over the course of several days; the results of two of these runs are shown in Table 3.1.

Results. As can be seen from Table 3.1 the results obtained were in general quite satisfactory, with the measure of agreement between the concentration of chlorine dioxide added and that which was determined by FIA being within one or two standard deviations. This experiment demonstrates that it should be possible to apply the FIA method to the analysis of chlorine dioxide in drinking water samples.

3.4.1 Summary of FIA Study

From the results obtained during the course of this work we have demonstrated that the two reagents amaranth and evans blue are suitable for use in a simple FIA system for the determination of chlorine dioxide in water. Amaranth would appear to be the reagent of choice because calibration curves obtained with this reagent at low levels (below 1 mg/L) of chlorine dioxide are more reproducible. Although amaranth has a lower absorbtivity than evans blue it is considerably cheaper, and is available from commercial suppliers in a purer form. In addition evans blue has received some attention as a possible carcinogen[111]. The detection limits for the two reagents under

Table 3.1

Analysis of Spiked Samples of Chlorine Dioxide in Tap water by FIA using Amaranth as the Reagent.

Run 1

Sample Number	ClO_2 added[1]	ClO_2 found	S_{sample}[2]
	(mg/L)	(mg/L)	
1	0.15	0.12	0.02
2	0.31	0.33	0.02

Run 2

Sample Number	ClO_2 added[1]	ClO_2 found	S_{sample}[2]
	(mg/L)	(mg/L)	
1	0.19	0.22	0.02
2	0.33	0.35	0.02

[1] Concentration of ClO_2 added determined by UV measurement

[2] Standard deviations (S_{sample}) were calculated using equation (2) on page 164

the optimum conditions determined during this work were of the order of 0.12 ± 0.03 mg/L. Although the majority of these experiments were carried out in distilled water, the results of the spiked sample experiments suggest that it should be possible to apply the method to treated water samples. Although no experiments were carried out in stilling basin water where sample turbidity can be a problem, it should in principle be possible to correct for turbidity as was done in the work on the colorimetric reagents in chapter 2. Finally, it should be pointed out that the results in this study were obtained using relatively unsophisticated apparatus. With a more sensitive detector, possibly one utilizing a laser, it should be possible to obtain considerably lower detection limits for this FIA system than were reported here.

Chapter 4

Summary of Results and Suggestions for Further Work

4.1.1 Sampling Study of the City of Edmonton Distribution System

The first part of this work involved a major sampling study of the City of Edmonton water distribution system. A number of sampling sites (consisting of the satellite reservoirs and city fire halls) were chosen and over the course of one calendar year from May 1988 to April 1989 the effect of several parameters including geographical location in the system and seasonal changes, on water quality in the distribution system were monitored. A total of fifteen chemical properties (including concentrations of six metals) were studied in this work, all of which are important to overall water quality. Two statistical studies using analysis of variance (ANOVA) were carried out to determine whether any differences could be observed between the quality of water produced at the two City of Edmonton water treatment plants, and also whether the pipe material through which the water flowed had any detrimental effect on water quality. In addition, studies were carried out to monitor water quality at two "dead-end" locations[7,8] where the flow of water was restricted, and also to assess the effect of the annual spring runoff on several chemical parameters.

Most of the year few variations were observed in the levels of the various chemical parameters studied (see appendix 1). This suggests that the treatment process is under satisfactory statistical control. Many of the parameters (although not the metals) are monitored by the city on a daily basis and are held within ranges determined by published guidelines[3]. Despite this, considerable variations in the levels of organic carbon, iron, copper and turbidity were observed during the runoff period. The organic carbon, which was monitored by a UV method developed by the Rossdale laboratory staff[26], increased dramatically during this time, and monitoring of this property proved to be a useful warning of potential water problems.

The source of the additional metals in the distribution system during spring runoff most likely arises from traces of these metals which are present as contaminants in the bulk chemicals which are used in the treatment process, since higher concentrations of these bulk chemicals are used during runoff to combat turbidity and color problems in the water. Possibly some metal-humic acid complexes[35-37] form during this time and pass into the distribution system; this possibility warrants further study. As a result of this study a program was initiated by the city to increase the level of metals analysis carried out on the bulk chemicals. We were also able to make additional recommendations to the City of Edmonton water laboratory regarding sampling of the distribution system, a number of which have been implemented. Although this study by and large found little variation in water quality, it provided an excellent "snapshot" of the state of the Edmonton water distribution system and should prove useful as a comprehensive baseline study to which further studies may be compared.

4.2.1 The Determination of Chlorine Dioxide in Drinking Water

In the second part of this project four existing methods for the analysis of chlorine dioxide, used as a primary disinfectant in the drinking water treatment process, were evaluated. The first two, spectrophotometric UV measurement and a four step amperometric titration procedure developed by Aieta and co-workers[66], are direct methods. The latter was developed for the determination of the composition of chlorine dioxide produced from commercial generators for water treatment and other industries. An initial study carried out in distilled water comparing the two methods revealed considerable discrepancies in the results obtained for identical standards of chlorine dioxide. An in-depth study of the Aieta method was undertaken and a number of problems associated with the method were identified and corrected. Following this a second comparison study was carried out. This time the results obtained for the two methods were comparable and we were confident of being able to accurately determine the concentrations of stock solutions and dilute standards of chlorine dioxide by either of these methods. The UV method, though simple and direct, is susceptible in real samples to interference from both organic and inorganic substances that absorb in the UV region.

The other two existing methods studied were colorimetric procedures. These were the chlorophenol red (CPR) method, developed initially by Wheeler and co-workers[70], and the acid chrome violet potassium (ACVK) method developed by Masschelein[72,73]. These are indirect procedures and stock chlorine dioxide solutions for calibration work must first be standardized by one of the methods previously mentioned. These colorimetric methods have both been previously applied to the determination of chlorine dioxide in various sample waters. However, much of the work on interferences in these methods was incomplete, especially for the CPR method. Therefore a full set of interference trials involving a number of species known to occur in varying concentrations in the City of Edmonton drinking water was carried out using both colorimetric as well as the Aieta and UV methods. The results of these interference tests indicated that while the CPR and ACVK methods had few serious interferences and could probably be used for the analysis of treated water samples, the Aieta method had several interferences, the biggest being that of chlorite. Since it can be expected that the level of chlorite (one of the major decomposition products of chlorine dioxide) in treated water will be much higher than the level of chlorine dioxide, the determination of a small amount of chlorine dioxide in a larger amount of chlorite is extremely difficult by this procedure. The UV method is essentially free of interference from chlorine-containing inorganics, but the high background absorbance of treated water prevents its use for the direct determination of chlorine dioxide in treated water. In practice the UV method could be used only as a method for standardizing chlorine dioxide standards in distilled water. Here it proved to be an excellent method.

Of the two colorimetric methods in the literature, the ACVK method in particular looked promising, for in addition to being essentially interference free, it was straightforward, required only a single reagent, and could be used in the pH range of the majority of treated water samples (between 8 and 9). However, because of the low absorbtivity of ACVK the quoted detection limit for this method is only 0.02 ± 0.01 mg/L[73]. This is not as good as chlorophenol red, which because of its much higher absorbtivity has a quoted detection limit of 0.005 ± 0.003 mg/L[71] a value, however, obtained using a specially designed 25-cm path length cell.

Possible replacements for ACVK were therefore sought which would be more sensitive and produce a detection limit for chlorine dioxide at least comparable or better than that obtained for CPR. To this end thirteen indicator reagents were selected and their properties evaluated. Of the compounds screened amaranth and evans blue showed considerable promise and were selected for further study. A second set of interference trials was carried out on these compounds using the same interference tests as before. The results were quite promising.

Since both sets of interference tests had been carried out in distilled water, the next logical step was to test and compare the performance of CPR, ACVK, amaranth and evans blue in treated water. As expected, no residual chlorine dioxide was found in samples taken from the distribution system. These experiments also showed no serious interferences from species present in the drinking water for any of the reagents (blank solutions containing only the reagent in both distilled and treated water had essentially the same absorbance). Therefore comparison studies were carried out using water from the stilling basins at the Rossdale water treatment plant where the chlorine dioxide is added and where the disinfection process takes place. However, since stilling basin is considerably more turbid than normal drinking water (due to the fact that the stilling basin water has not passed through the anthracite filters which removes most of the particulate matter responsible for the increased sample turbidity), it was necessary to determine the effects of sample turbidity on solutions containing the various reagents. Additional "ruggedness" experiments were also performed to determine the effects of time and sample temperature.

Chlorine dioxide spikes over the range 0 to 0.3 mg/L in stilling basin water were used to assess the relative performances of each of the indicators. The results obtained were generally satisfactory. Below 0.03 mg/L of chlorine dioxide ACVK is not sufficiently sensitive to be useful. A second study was carried out using amaranth, evans blue and chlorophenol red (CPR) on spiked standards ranging from 0.02 to 0.1 mg/L). Finally, these three indicators were used to analyze samples taken very close to the point of addition of chlorine dioxide. Good agreement among the three reagents for the concentration of the samples was obtained.

From the results of these experiments it appears that both amaranth and evans blue as developed during the course of this work can be successfully used for the determination of trace levels of ClO_2 in drinking water samples. Of the two, evans blue is more sensitive due to its higher absorbtivity value of 86.50 ± 0.90 L g^{-1} cm^{-1}, (amaranth has an absorbtivity of 38.09 ± 0.46 L g^{-1} cm^{-1}). However, amaranth is available from commercial suppliers in a more pure form than evans blue and is also cheaper by about a factor of five. In addition, evans blue is reported to be a possible carcinogen. The detection limits for chlorine dioxide are 0.005 ± 0.003 mg/L for amaranth and 0.004 ± 0.002 for evans blue, in a 10-cm path length cell. These detection limits are comparable to the quoted detection limit of chlorophenol red (CPR), given earlier and verified in this work. However, the CPR method has a number of disadvantages. The first being that three reagents are required for the method which must be added in a specific order to obtain optimum results. A second disadvantage is that the optimum pH for the CPR-chlorine dioxide reaction is 5 to 5.5. This is not within the normal range of the majority of municipal drinking waters, and a buffer is therefore required to bring the sample into the correct pH range. A third is that the CPR method also suffers interference from several species such as free chlorine and metal ions. Finally, the absorbance of solutions containing mixtures of CPR-ClO_2 vary with temperature, which requires that all solutions must be kept at at approximately the same temperature prior to analysis.

It should be possible to utilize the reagents developed in this work in the field, since both require only a single reagent and the minimum of ancillary equipment. Several portable spectrophotometers now commercially available (such as the Hach 2000 DR) make it possible to store several programs for standard calibration curves covering a wide range of concentrations. One possible application would be to carry out some further studies of the concentration profile of chlorine dioxide in the stilling basins at the Rossdale water treatment plant.

A second possible application is the determination of ClO_2 concentrations produced by industrial generators. This may be possible, for example for the generator at the satellite plant (# 3) at the Rossdale site. The concentrations produced by this small generator are of the order of 100 to 150 mg/L of chlorine dioxide. These concentrations could be determined by amaranth (after appropriate dilution) and compared to values determined by the amperometric titration method[66] currently used. This provides a check on the amperometric titration procedure.

4.3.1 The Application of Flow Injection Analysis (FIA) to the Determination of Chlorine Dioxide in Water

In the final part of this work a simple flow injection analysis (FIA)[114] system was designed and constructed for the determination of chlorine dioxide using either amaranth and evans blue as the carrier reagent. By varying the FIA parameters such as flow rate and length of the delay coil it was found that linear calibration curves could be obtained over various ranges of standards of chlorine dioxide. Use of a Rheodyne rotary injection valve with an external sampling loop enabled us to inject larger volumes of sample into the flow of carrier and increase the sensitivity of the system. Under the appropriate conditions, with a sample injection volume of approximately 70 μL it was possible to obtain detection limits of approximately 0.12 ± 0.03 using amaranth as the carrier reagent. Similar detection limits could be obtained with evans blue, although calibration curves using this reagent as carrier were not generally as reliable as those obtained for amaranth. Amaranth was overall the reagent of choice for the reasons outlined earlier in this chapter (and in chapter 3). As the previous experiments were carried out in distilled water, spiking experiments similar to those carried out earlier for the comparison studies in chapter 2 were performed in treated tap water. The results were satisfactory, and indicated that this method is applicable to the analysis of treated water samples.

Some work remains before this method can be considered for routine analysis. For example, no experiments were carried out on water from the stilling basins and no "real" sample analysis was done because of concern over the effects of sample turbidity. The detection limits achieved were good but not as high as those obtained by static spectrophotometry, primarily because of the smaller cell size used in FIA. It should be possible to decrease the detection limits by the use of a more sensitive detection system, possibly one based on a laser.

As it seems that the use of chiorine dioxide as a disinfectant in water treatment will continue to increase, a long term goal would be to produce a continuous analyzer based on FIA for the determination of chlorine dioxide in the field. In principle this should be possible using a portable spectrophotometer as a detector. The sample could be prefiltered to remove turbidity before being brought into contact with the carrier. Such a device would be a useful addition to the arsenal of instrumentation available for chlorine dioxide analysis and could find a number of applications as an on line monitor both in the water treatment industry and elsewhere.

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Appendix 1

Raw Data for the City of Edmonton Water Distribution System Study

This appendix contains the raw data collected during the sampling project on the City of Edmonton water distribution system. The first part of the appendix shows the dates on which samples were collected from the reservoirs and fire halls over the course of the study. This is followed by the results of the analyses carried out on the samples for the various chemical parameters monitored in this work. As stated earlier (see chapter 1) these parameters can be classified into two categories i.e non-metals and metals and the data is presented (chronologically) in accordance with this classification in the following order:

Reservoir non-metals data
Reservoir metals data
Fire Hall non-metals data
Fire hall metals data

Also contained in this appendix are the cumulative monthly averages (together with their associated standard deviations) which were calculated for the reservoirs and fire halls (see chapter 1 for details) for all the parameters studied in this work. A number of plots of average concentration against time (in months) for selected parameters are also shown.

Reservoir Sample Collection Dates (1988)

Reservoir	May	June	July	August	September	October	November	December
	(date)	(date)	(date)	(date)	(date)	(date)	(date)	(date)
Clareview	20 th	17 th	14 th	16 th	22 nd	20 th	17 th	16 th
Papaschase #1	13 th	9 th	7 th	9 th	29 th	18 th	10 th	9 th
Papaschase #2	13 th	9 th	7 th	9 th	29 th	18 th	26 th	9 th
Kaskitayo	13 th	9 th	7 th	11 th	29 th	13 th	10 th	9 th
Castledowns	19 th	17 th	29 th	10 th	22 nd	20 th	17 th	16 th
North Jasper Place	19 th	17 th	14 th	10 th	22 nd	20 th	17 th	16 th
Rosslyn # 1	20 th	17 th	29 th	15 th	26 th	20 th	17 th	16 th
Rosslyn # 2 *	20 th	17 th	29 th	15 th	26 th			
Millwoods	13 th	9 th	7 th	11 th	29 th	20 th	10 th	9 th
Thorncliff	13 th	9 th	7 th	8 th	29 th	13 th	10 th	9 th
Ormsby	13 th	9 th	7 th	8 th	29 th	13 th	10 th	9 th
Burnewood **	13 th	9 th	7 th		29 th	18 th	10 th	9 th
Londonderry	20 th	17 th	14 th	16 th	22 nd	20 th	17 th	16 th

* Rosslyn # 2 Reservoir was out of service from October to December.

** No sample was taken from the Burnewood booster station during the month of August.

Reservoir Sample Collection Dates (1989)

Reservoir	January	February	March	April
	(date)	(date)	(date)	(date)
Clareview	12 th	23 rd	9 th	20 th
Papaschase #1	21 st	3 rd	17 th	19 th
Papaschase #2	19 th	3 rd	17 th	19 th
Kaskitayo	21 st	3 rd	16 th	13 th
Castledowns	21 st	23 rd	9 th	6 th
North Jasper Place	12 th	24 th	9 th	6 th
Rosslyn # 1	12 th	23 rd	9 th	6 th
Rosslyn # 2 *		23 rd	9 th	6 th
Millwoods	19 th	3 rd	16 th	13 th
Thorncliff	19 th	3 rd	9 th	13 th
Ormsby	19 th	3 rd	9 th	13 th
Burnewood	19 th	3 rd	16 th	14 th
Londonderry	12 th	23 rd	9 th	20 th

* Rosslyn # 2 Reservoir was out of service for the month of January.

Fire Hall Sample Collection Dates (1988)

Fire Hall	May	June	July	September	October	November	December
	(date)	(date)	(date)	(date)	(date)	(date)	(date)
# 1	31 st	29 th	14 th	21 st	20 th	30 th	23 rd
# 2	31 st	29 th	14 th	21 st	20 th	30 th	23 rd
# 3	26 th	24 th	21 st	21 st	18 th	26 th	22 nd
# 4	19 th	27 th	14 th	30 th	13 th	17 th	17 th
# 5 **	20.th		15 th	20 th	19 th	30 th	22 nd
# 6	26 th	24 th	22 nd	21 st	13 th	26 th	23 rd
# 7	20.th	29 th	14 th	28 th	28 th	17 th	17 th
# 8 **	19 th		14 th	30 th	18 th	30 th	17 th
# 9	26 th	24 th	22 nd	30 th	18 th	26 th	23 rd
# 10	20.th	2 nd	15 th	21 st	28 th	17 th	17 th
# 11 *		3 rd	21 st	28 th	18 th	30 th	17 th
# 12	26 th	27 th	21 st	28 th	13 th	28 th	21 st
# 13	26 th	24 th	21 st	30 th	13 th	28 th	23 rd
# 15	27 th	24 th	22 nd	21 st	13 th	26 th	23 rd
# 16	26 th	24 th	22 nd	20 th	18 th	28 th	23 rd
# 17	19 th	29 th	15 th	30 th	28 th	17 th	17 th
# 19 **	26 th		22 nd	21 st	13 th	26 th	21 st
# 20	26 th	24 th	21 st	26 th	13 th	28 th	22 nd
# 22	31 st	27 th	29 th	21 st	22 nd	30 th	23 rd
# 23 *		2 nd	14 th	28 th	13 th	17 th	17 th
# 24 *		2 nd	15 th	30 th	20 th	30 th	22 nd

* No samples were collected from Fire Halls # 11, # 23 and # 24 during the month of May.

** No samples were collected from Fire Halls # 5, # 8 and # 19 during the month of June.

Fire Hall Sample Collection Dates (1989)

Fire Hall	January	February	March	April
	(date)	(date)	(date)	(date)
# 1	24 th	24 th	23 rd	27 th
# 2	24 th	21 st	23 rd	27 th
# 3	26 th	21 st	24 th	13 th
# 4	12 th	24 th	23 rd	21 st
# 5	24 th	23 rd	23 rd	20 th
# 6	20 th	22 nd	17 th	13 th
# 7	26 th	23 rd	22 nd	20 th
# 8	12 th	23 rd	23 rd	21 st
# 9	20 th	22 nd	16 th	14 th
# 10	12 th	23 rd	23 rd	20 th
# 11	29 th	23 rd	16 th	20 th
# 12	21 st	21 st	16 th	13 th
# 13	20 th	22 nd	16 th	13 th
# 15	20 th	22 nd	17 th	13 th
# 16	20 th	29 th	16 th	14 th
# 17	12 th	23 rd	23 rd	20 th
# 19	21 st	21 st	16 th	13 th
# 20	21 st	22 nd	16 th	13 th
# 22	26 th	21 st	23 rd	21 st
# 23	12 th	24 th	23 rd	21 st
# 24	26 th	23 rd	23 rd	20 th

Reservoir Non Metals Data (May 1988)

Reservoir	Total Chloramines	Total Oxidants	Fluoride Ion	pH	Turbidity	Total Hardness	Calcium Hardness	Total Alkalinity	Organic Carbon
	(ppm)	(ppm)	(ppm)		(NTU)	(ppm)	(ppm)	(ppm)	(HAU)
Clareview	1.94	0.37	1.02	8.2	0.15	124	72	62	2.8
Papaschase #1	2.08	0.22	1.03	8.2	0.35	113	69	57	3.2
Papaschase #2	2.06	0.25	1.03	8.3	0.10	115	69	57	2.2
Kaskitayo	2.07	0.29	1.00	8.2	0.15	110	68	51	2.0
Castledowns	1.98	0.34	0.99	8.2	0.10	115	68	49	2.0
North Jasper	1.95	0.26	0.96	8.2	0.10	112	68	49	2.5
Rosslyn # 1	2.07	0.34	1.00	8.2	0.50	120	72	61	2.1
Rosslyn # 2	2.03	0.26	1.04	8.2	0.10	118	73	58	2.2
Millwoods	2.00	0.30	1.02	8.3	0.10	113	65	53	1.8
Thorncliff	2.05	0.29	1.03	8.3	0.10	113	66	47	3.2
Ormsby	2.07	0.26	1.00	8.2	0.10	118	68	47	2.2
Burnewood	1.96	0.27	1.02	8.2	0.15	116	71	52	2.2
Londonderry	1.92	0.35	1.02	8.1	0.10	125	73	64	2.9

Reservoir Non Metals Data (June 1988)

Reservoir	Total Chloramines	Total Oxidants	Fluoride Ion	pH	Turbidity	Total Hardness	Calcium Hardness	Total Alkalinity	Organic Carbon
	(ppm)	(ppm)	(ppm)		(NTU)	(ppm)	(ppm)	(ppm)	(HAU)
Clareview	1.93	0.35	1.02	8.0	0.10	116	68	61	2.4
Papaschase #1	1.99	0.26	0.99	8.2	0.15	114	69	59	2.1
Papaschase #2	1.95	0.26	0.98	8.2	0.05	114	70	55	2.1
Kaskitayo	1.96	0.24	0.99	8.2	0.05	113	64	50	1.2
Castledowns	1.99	0.32	1.02	8.3	0.05	117	69	47	2.0
North Jasper	2.01	0.29	1.01	8.2	0.05	116	69	48	1.8
Rosslyn # 1	2.00	0.33	1.00	8.1	0.10	117	69	58	2.3
Rosslyn # 2	2.01	0.25	1.02	8.1	0.10	116	70	58	2.4
Millwoods	1.90	0.24	0.99	8.2	0.05	111	65	53	1.4
Thorncliff	2.05	0.26	0.98	8.3	0.10	108	64	48	1.6
Ormsby	1.90	0.26	0.98	8.2	0.05	110	64	49	1.4
Burnewood	2.03	0,19	0.98	8.2	0.15	112	66	49	2.3
Londonderry	1.95	0.32	1.03	8.0	0.05	117	68	51	3.2

Reservoir Non Metals Data (July 1988)

Reservoir	Total Chloramines	Total Oxidants	Fluoride Ion	pH	Turbidity	Total Hardness	Calcium Hardness	Total Alkalinity	Organic Carbon
	(ppm)	(ppm)	(ppm)		(NTU)	(ppm)	(ppm)	(ppm)	(HAU)
Clareview	1.98	0.33	1.00	8.2	0.10	121	70	47	3.6
Papaschase #1	1.82	0.32	1.02	8.2	0.10	113	69	48	3.3
Papaschase #2	1.98	0.18	1.01	8.2	0.15	110	68	48	3.1
Kaskitayo	1.96	0.28	1.03	8.2	0.05	110	67	47	2.6
Castledowns	2.03	0.29	1.08	8.2	0.15	114	69	43	2.5
North Jasper	1.93	0.16	0.97	8.2	0.10	117	74	48	3.6
Rosslyn # 1	1.90	0.24	1.00	8.2	0.05	113	71	48	3.9
Rosslyn # 2	2.01	0.20	1.03	8.2	0.20	114	75	43	3.4
Millwoods	1.96	0.29	1.03	8.2	0.05	111	68	47	2.9
Thorncliff	2.02	0.27	1.01	8.3	0.10	110	67	48	2.5
Ormsby	1.91	0.29	1.01	8.3	0.10	112	67	46	2.2
Burnewood	1.94	0.27	0.99	8.2	0.10	118	68	46	2.4
Londonderry	1.88	0.29	0.97	8.2	0.15	117	68	47	3.4

Reservoir Non Metals Data (August 1988)

Reservoir	Total Chloramines	Total Oxidants	Fluoride Ion	pH	Turbidity	Total Hardness	Calcium Hardness	Total Alkalinity	Organic Carbon
	(ppm)	(ppm)	(ppm)		(NTU)	(ppm)	(ppm)	(ppm)	(HAU)
Clareview	1.92	0.28	1.00	8.3	0.10	112	68	54	4.6
Papaschase #1	1.95	0.32	1.04	8.2	0.10	117	71	60	4.9
Papaschase #2	1.85	0.31	1.01	8.2	0.05	114	69	60	4.4
Kaskitayo	1.80	0.28	1.00	8.3	0.10	112	70	46	3.7
Castledowns	1.90	0.26	0.90	8.4	0.10	118	72	48	4.3
North Jasper	1.85	0.27	0.91	8.3	0.10	118	74	50	4.2
Rosslyn # 1	1.74	0.31	1.01	8.3	0.10	113	67	52	4.5
Rosslyn # 2	1.74	0.31	1.02	8.3	0.10	112	67	51	4.5
Millwoods	1.88	0.27	1.01	8.2	0.05	112	70	48	3.8
Thorncliff	1.80	0.29	1.01	8.2	0.10	118	74	52	4.4
Ormsby	1.85	0.28	1.00	8.2	0.05	111	72	48	4.2
Burnewood *									
Londonderry	1.87	0.31	1.00	8.2	0.10	109	64	55	4.8

* No sample was collected from the Burnewood booster station during the month of August.

Reservoir Non Metals Data (September 1988)

Reservoir	Total Chloramines	Total Oxidants	Fluoride Ion	pH	Turbidity	Total Hardness	Calcium Hardness	Total Alkalinity	Organic Carbon
	(ppm)	(ppm)	(ppm)		(NTU)	(ppm)	(ppm)	(ppm)	(HAU)
Clareview	1.72	0.30	1.01	8.2	0.10	113	71	60	2.7
Papaschase #1	1.81	0.28	1.01	8.2	0.20	116	72	55	3.6
Papaschase #2	1.97	0.27	1.01	8.3	0.20	111	72	55	3.1
Kaskitayo	1.87	0.27	1.01	8.3	0.25	111	71	55	2.8
Castledowns	1.93	0.30	0.99	8.4	0.05	110	69	56	2.3
North Jasper	1.83	0.28	0.97	8.3	0.10	110	69	57	2.9
Rosslyn # 1	1.80	0.29	0.98	8.3	0.15	112	68	55	3.0
Rosslyn # 2	1.82	0.30	0.99	8.2	0.30	114	69	56	3.2
Millwoods	1.99	0.25	1.00	8.3	0.30	109	73	59	3.9
Thorncliff	2.05	0.26	1.01	8.3	0.20	112	73	55	2.7
Ormsby	2.00	0.22	0.99	8.3	0.25	112	70	53	2.7
Burnewood	1.90	0.30	1.00	8.3	0.60	113	73	58	3.2
Londonderry	1.91	0.31	1.01	8.2	0.05	115	68	63	3.0

Reservoir Non Metals Data (October 1988)

Reservoir	Total Chloramines	Total Oxidants	Fluoride Ion	pH	Turbidity	Total Hardness	Calcium Hardness	Total Alkalinity	Organic Carbon
	(ppm)	(ppm)	(ppm)		(NTU)	(ppm)	(ppm)	(ppm)	(HAU)
Clareview	2.01	0.26	0.95	8.3	0.30	116	71	60	2.8
Papaschase #1	1.75	0.30	0.98	8.3	0.10	116	71	57	2.1
Papaschase #2	1.89	0.30	1.02	8.3	0.15	111	72	59	1.9
Kaskitayo	1.94	0.36	0.97	8.3	0.15	115	71	53	2.5
Castledowns	2.01	0.34	0.97	8.4	0.25	114	67	53	2.3
North Jasper	1.98	0.31	0.94	8.4	0.10	116	70	55	2.5
Rosslyn # 1	1.89	0.30	0.99	8.3	0.20	115	71	66	3.1
Rosslyn # 2 *									
Millwoods	1.87	0.36	0.99	8.4	0.15	113	74	56	2.8
Thorncliff	1.95	0.30	0.99	8.3	0.25	106	69	53	3.2
Ormsby	1.96	0.33	1.00	8.3	0.15	111	70	53	2.7
Burnewood	1.91	0.37	0.99	8.4	0.30	115	72	56	2.4
Londonderry	1.98	0.36	0.95	8.3	0.40	116	71	60	2.6

* Rosslyn # 2 Reservoir was out of service for the month of October.

Reservoir Non Metals Data (November 1988)

Reservoir	Total Chloramines	Total Oxidants	Fluoride Ion	pH	Turbidity	Total Hardness	Calcium Hardness	Total Alkalinity	Organic Carbon
	(ppm)	(ppm)	(ppm)		(NTU)	(ppm)	(ppm)	(ppm)	(HAU)
Clareview	1.86	0.30	1.02	8.1	0.30	115	69	68	3.0
Papaschase #1	1.93	0.39	1.03	8.4	0.35	110	69	51	2.7
Papaschase #2	2.01	0.23	1.01	8.4	0.40	107	62	50	2.1
Kaskitayo	1.93	0.36	1.01	8.4	0.30	110	70	52	2.2
Castledowns	2.03	0.26	1.01	8.5	0.15	110	72	63	2.6
North Jasper	2.01	0.27	1.00	8.4	0.15	108	68	60	1.9
Rosslyn # 1	1.99	0.29	1.00	8.3	0.30	111	67	62	2.7
Rosslyn # 2 *									
Millwoods	1.95	0.33	0.95	8.4	0.30	109	71	51	2.3
Thorncliff	1.99	0.31	0.96	8.5	0.35	110	71	60	2.2
Ormsby	1.98	0.39	0.97	8.4	0.25	109	69	52	2.6
Burnewood	1.97	0.25	0.94	8.4	0.45	110	67	51	2.1
Londonderry	1.98	0.27	1.03	8.3	0.35	118	70	67	2.8

* Rosslyn # 2 Reservoir was out of service for the month of November.

Reservoir Non Metals Data (December 1988)

Reservoir	Total Chloramines	Total Oxidants	Fluoride Ion	pH	Turbidity	Total Hardness	Calcium Hardness	Total Alkalinity	Organic Carbon
	(ppm)	(ppm)	(ppm)		(NTU)	(ppm)	(ppm)	(ppm)	(HAU)
Clareview	2.01	0.26	0.99	8.4	0.25	115	61	64	2.3
Papaschase #1	1.88	0.27	1.00	8.4	0.50	110	62	55	1.3
Papaschase #2	1.92	0.31	0.98	8.4	0.40	104	64	43	1.6
Kaskitayo	1.94	0.28	0.99	8.4	0.35	105	62	44	1.0
Castledowns	1.89	0.31	0.98	8.5	0.35	108	64	53	2.1
North Jasper	1.87	0.28	1.02	8.5	0.25	107	63	48	1.8
Rosslyn # 1	1.90	0.29	1.01	8.4	0.40	113	61	54	2.2
Rosslyn # 2 *									
Millwoods	1.95	0.31	0.99	8.4	0.15	102	62	42	1.1
Thorncliff	1.98	0.29	1.01	8.4	0.35	112	64	48	1.6
Ormsby	1.94	0.29	1.04	8.4	0.20	110	66	48	1.2
Burnewood	1.95	0.26	0.97	8.4	0.40	105	62	44	1.1
Londonderry	1.90	0.30	1.02	8.5	0.20	105	66	46	1.7

* Rosslyn # 2 Reservoir was out of service for the month of December.

Reservoir Non Metals Data (January 1989)

Reservoir	Total Chloramines	Total Oxidants	Fluoride Ion	pH	Turbidity	Total Hardness	Calcium Hardness	Total Alkalinity	Organic Carbon
	(ppm)	(ppm)	(ppm)		(NTU)	(ppm)	(ppm)	(ppm)	(HAU)
Clareview	1.93	0.21	1.00	8.4	0.55	110	58	58	3.9
Papaschase #1	1.94	0.28	1.02	8.5	0.20	114	62	60	3.7
Papaschase #2	1.86	0.21	1.01	8.5	0.15	110	64	60	3.5
Kaskitayo	1.96	0.26	1.01	8.5	0.15	120	67	59	3.8
Castledowns	1.97	0.23	1.00	8.5	0.10	111	64	57	3.3
North Jasper	1.86	0.24	1.00	8.2	0.20	115	64	56	3.1
Rosslyn # 1	1.95	0.24	0.99	8.4	0.30	111	62	56	3.7
Rosslyn # 2 *									
Millwoods	1.99	0.26	1.02	8.5	0.15	117	66	56	3.2
Thorncliff	1.96	0.27	1.01	8.5	0.25	115	67	58	3.3
Ormsby	1.95	0.27	1.03	8.4	0.10	111	64	57	3.2
Burnewood	1.93	0.26	1.01	8.5	0.15	112	64	55	3.5
Londonderry	1.96	0.24	0.96	8.4	0.15	111	59	61	3.8

* Rosslyn # 2 Reservoir was out of service for the month of January.

Reservoir Non Metals Data (February 1989)

Reservoir	Total Chloramines	Total Oxidants	Fluoride Ion	pH	Turbidity	Total Hardness	Calcium Hardness	Total Alkalinity	Organic Carbon
	(ppm)	(ppm)	(ppm)		(NTU)	(ppm)	(ppm)	(ppm)	(HAU)
Clareview	1.94	0.27	0.99	8.5	0.15	112	61	57	3.4
Papaschase #1	1.93	0.30	0.97	8.5	0.30	113	63	54	3.6
Papaschase #2	1.91	0.32	0.98	8.5	0.30	114	62	53	3.5
Kaskitayo	1.96	0.29	0.98	8.5	0.15	111	63	53	3.5
Castledowns	1.91	0.32	1.02	8.5	0.10	116	66	49	3.4
North Jasper	1.93	0.30	1.03	8.3	0.15	113	67	52	3.8
Rosslyn # 1	1.95	0.26	0.98	8.5	0.20	116	62	54	3.7
Rosslyn # 2	1.97	0.27	1.00	8.5	0.20	114	60	55	3.5
Millwoods	2.00	0.29	0.99	8.5	0.15	112	66	53	3.5
Thorncliff	1.99	0.28	1.00	8.5	0.20	112	67	54	3.6
Ormsby	1.98	0.29	0.96	8.5	0.25	112	64	52	3.4
Burnewood	1.93	0.29	1.01	8.4	0.30	112	66	54	3.5
Londonderry	1.96	0.27	1.00	8.4	0.10	118	61	57	3.7

Reservoir Non Metals Data (March 1989)

Reservoir	Total Chloramines	Total Oxidants	Fluoride Ion	pH	Turbidity	Total Hardness	Calcium Hardness	Total Alkalinity	Organic Carbon
	(ppm)	(ppm)	(ppm)		(NTU)	(ppm)	(ppm)	(ppm)	(HAU)
Clareview	2.05	0.25	0.97	8.4	0.10	113	60	57	4.4
Papaschase #1	1.94	0.27	0.96	8.4	0.30	118	64	57	4.4
Papaschase #2	1.90	0.27	0.97	8.5	0.15	117	66	43	2.6
Kaskitayo	1.97	0.33	1.00	8.3	0.10	113	70	43	3.2
Castledowns	2.02	0.26	0.97	8.4	0.10	112	67	55	3.2
North Jasper	2.03	0.26	1.00	8.4	0.20	112	68	54	3.8
Rosslyn # 1	1.88	0.27	0.99	8.3	0.10	113	62	55	3.7
Rosslyn # 2	1.87	0.28	1.00	8.3	0.10	113	67	56	3.8
Millwoods	1.96	0.30	1.02	8.4	0.05	112	67	44	3.0
Thorncliff	1.97	0.28	1.02	8.5	0.10	112	70	49	3.3
Ormsby	1.97	0.27	0.97	8.3	0.10	112	66	53	3.6
Burnewood	1.96	0.31	1.00	8.4	0.05	110	71	44	3.4
Londonderry	2.04	0.27	0.98	8.4	0.10	118	65	60	4.2

Reservoir Non Metals Data (April 1989)

Reservoir	Total Chloramines	Total Oxidants	Fluoride Ion	pH	Turbidity	Total Hardness	Calcium Hardness	Total Alkalinity	Organic Carbon
	(ppm)	(ppm)	(ppm)		(NTU)	(ppm)	(ppm)	(ppm)	(HAU)
Clareview	1.83	0.25	0.99	8.4	0.35	119	65	58	4.3
Papaschase #1	1.87	0.31	0.98	8.4	0.40	109	72	44	8.5
Papaschase #2	1.88	0.26	1.00	8.4	0.15	111	74	43	10.0
Kaskitayo	1.93	0.31	1.04	8.4	0.15	109	74	42	10.7
Castledowns	1.91	0.30	1.00	8.5	0.15	108	72	43	4.7
North Jasper	1.90	0.31	0.95	8.2	0.10	113	72	42	3.9
Rosslyn # 1	1.85	0.30	0.96	8.4	0.15	119	70	51	4.7
Rosslyn # 2	1.83	0.24	0.96	8.4	0.40	114	66	56	3.8
Millwoods	1.91	0.30	1.02	8.4	0.15	110	72	44	10.3
Thorncliff	1.99	0.27	0.99	8.4	0.15	108	72	43	9.2
Ormsby	1.90	0.31	1.00	8.5	0.10	111	76	41	9.4
Burnewood	1.90	0.31	1.03	8.3	0.20	110	74	44	10.8
Londonderry	1.90	0.34	1.02	8.2	0.20	120	77	45	7.5

Reservoir Metals Data (June 1988)

Reservoir	Aluminium	Cadmium	Chromium	Copper	Iron	Lead
	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)
Clareview	210	0.1	0.4	1	7	1.1
Papaschase # 1	180	0.0	0.4	1	4	0.5
Papaschase # 2	210	0.0	0.5	2	5	1.1
Kaskitayo	200	0.1	0.5	2	6	1.4
Castledowns	180	0.3	0.6	1	2	2.6
North Jasper	170	0.2	0.6	1	15	2.0
Rosslyn # 1	220	0.1	0.5	1	40 *	10.1
Rosslyn # 2	220	0.1	0.5	1	8	1.5
Millwoods	200	0.0	0.5	2	4	1.1
Thorncliff	200	0.0	0.5	0	13	1.1
Ormsby	190	0.1	0.5	1	5	1.3
Burnewood	180	0.1	1.8	2	3	0.9
Londonderry	170	0.2	0.5	2	17	1.0

* Original sample diluted x10 prior to analysis.

Note All Aluminium values were obtained after a ten fold dilution of the original sample prior to analysis.

Reservoir Metals Data (July 1988)

Reservoir	Aluminium	Cadmium	Chromium	Copper	Iron	Lead
	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)
Clareview	250	0.1	0.5	1	6	0.8
Papaschase # 1	240	0.0	0.5	1	5	0.9
Papaschase # 2	240	0.0	0.5	1	5	0.9
Kaskitayo	230	0.1	0.5	1	11	1.0
Castledowns	240	0.1	0.6	2	3	0.8
North Jasper	230	0.2	0.6	2	13	0.8
Rosslyn # 1	250	0.1	0.5	2	40 *	0.7
Rosslyn # 2	250	0.1	0.5	2	10	0.7
Millwoods	270	0.0	0.6	2	11	1.0
Thorncliff	190	0.0	0.5	0	8	0.9
Ormsby	200	0.1	0.6	1	12	1.4
Burnewood	230	0.1	0.5	2	5	1.6
Londonderry	240	0.1	0.5	2	10	0.7

* By dilution (x10) of the original sample.

Note All Aluminium values were obtained after a ten fold dilution of the original sample prior to analysis.

Reservoir Metals Data (September 1988)

Reservoir	Aluminium	Cadmium	Chromium	Copper	Iron	Lead
	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)
Clareview	380	0.1	0.6	3	5	0.7
Papaschase # 1	360	0.1	0.6	2	9	0.8
Papaschase # 2	310	0.1	0.7	1	6	0.9
Kaskitayo	340	0.1	0.5	1	12	0.8
Castledowns	370	0.2	0.6	1	1	0.7
North Jasper	390	0.1	0.7	2	11	0.8
Rosslyn # 1	410	0.1	0.5	2	30 *	0.9
Rosslyn # 2	400	0.1	0.5	1	4	1.0
Millwoods	350	0.2	0.6	3	6	0.8
Thorncliff	360	0.1	0.6	1	8	0.7
Ormsby	370	0.2	0.7	2	13	0.9
Burnewood	350	0.1	0.6	4	4	0.8
Londonderry	410	0.1	0.5	2	7	0.7

* Original sample diluted x10 prior to analysis.

Note All Aluminium values were obtained after a ten fold dilution of the original sample prior to analysis.

Reservoir Metals Data (October 1988)

Reservoir	Aluminium	Cadmium	Chromium	Copper	Iron	Lead
	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)
Clareview	310	0.1	0.6	7	9	0.7
Papaschase # 1	450	0.1	0.7	6	13	0.7
Papaschase # 2	350	0.1	0.8	2	7	0.5
Kaskitayo	330	0.3	0.8	7	14	0.8
Castledowns	230	0.2	0.5	2	2	0.7
North Jasper	270	0.2	0.5	3	14	0.7
Rosslyn # 1	400	0.2	0.5	6	20	0.8
Rosslyn # 2 *						
Millwoods	410	0.2	1.0	10	6	0.8
Thorncliff	320	0.1	0.8	6	15	0.7
Ormsby	360	0.1	0.8	6	15	1.0
Burnewood	430	0.1	0.9	7	13	0.9
Londonderry	360	0.1	0.5	8	9	0.5

* Rosslyn # 2 Reservoir was out of service for the month of October.

Note All Aluminium values were obtained after a ten fold dilution of the original sample prior to analysis.

Reservoir Metals Data (November 1988)

Reservoir	Aluminium	Cadmium	Chromium	Copper	Iron	Lead
	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)
Clareview	420	0.2	0.4	1	5	0.5
Papaschase # 1	420	0.2	0.5	3	4	0.7
Papaschase # 2	480	0.3	0.6	1	15	0.9
Kaskitayo	480	0.3	0.5	1	7	0.6
Castledowns	550	0.3	0.7	2	1	0.6
North Jasper	460	0.2	0.5	1	17	0.7
Rosslyn # 1	440	0.3	0.5	1	40 **	1.4
Rosslyn # 2 *						
Millwoods	500	0.2	0.4	1	4	0.6
Thorncliff	540	0.2	0.4	2	7	0.5
Ormsby	640	0.6	0.6	1	8	0.5
Burnewood	510	0.3	0.4	9	30 **	8.2
Londonderry	400	0.3	0.4	1	11	0.5

* Rosslyn # 2 Reservoir was out of service for the month of November.

** Original sample diluted x10 prior to analysis.

Note All Aluminium values were obtained after a ten fold dilution of the original sample prior to analysis.

Reservoir Metals Data (December 1988)

Reservoir	Aluminium	Cadmium	Chromium	Copper	Iron	Lead
	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)
Clareview	270	0.1	0.3	1	5	0.7
Papaschase # 1	380	0.1	0.7	2	40 **	0.7
Papaschase # 2	260	0.1	0.5	1	4	0.8
Kaskitayo	450	0.2	0.5	0	7	0.9
Castledowns	370	0.1	0.5	1	3	1.0
North Jasper	280	0.1	0.4	0	10	0.8
Rosslyn # 1	310	0.1	0.4	2	40 **	0.8
Rosslyn # 2 *						
Millwoods	310	0.1	0.5	1	8	0.7
Thorncliff	270	0.3	0.4	1	12	0.7
Ormsby	260	0.1	0.5	2	6	0.8
Burnewood	450	0.2	0.6	5	13	0.8
Londonderry	390	0.1	0.7	1	8	0.8

* Rosslyn # 2 Reservoir was out of service for the month of December.

** Original sample diluted x10 prior to analysis.

Note All Aluminium values were obtained after a ten fold dilution of the original sample prior to analysis.

Reservoir Metals Data (January 1989)

Reservoir	Aluminium (ppb)	Cadmium (ppb)	Chromium (ppb)	Copper (ppb)	Iron (ppb)	Lead (ppb)
Clareview	440	0.2	0.5	4	10	1.0
Papaschase # 1	460	0.2	0.7	1	1	1.1
Papaschase # 2	460	0.1	0.7	1	1	1.1
Kaskitayo	450	0.2	0.7	2	2	1.2
Castledowns	430	0.2	0.6	1	1	1.0
North Jasper	460	0.2	0.6	1	3	1.1
Rosslyn # 1	480	0.2	0.6	3	6	1.0
Rosslyn # 2 *						
Millwoods	480	0.1	0.7	3	2	1.0
Thorncliff	480	0.2	0.8	1	5	1.1
Ormsby	430	0.1	0.7	1	3	1.1
Burnewood	440	0.1	0.7	1	2	1.0
Londonderry	420	0.2	0.6	1	2	1.2

* Rosslyn # 2 reservoir was out of service for the month of January.

Note All Aluminium values were obtained after a ten fold dilution of the original sample prior to analysis.

Reservoir Metals Data (February 1989)

Reservoir	Aluminium	Cadmium	Chromium	Copper	Iron	Lead
	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)
Clareview	330	0.1	0.7	1	3	0.9
Papaschase # 1	280	0.1	0.6	1	40 *	0.9
Papaschase # 2	270	0.1	0.6	1	5	0.9
Kaskitayo	280	0.1	0.5	0	12	0.9
Castledowns	340	0.1	0.7	1	2	0.8
North Jasper	320	0.1	0.9	0	2	0.9
Rosslyn # 1	310	0.1	0.6	1	10	0.9
Rosslyn # 2	310	0.1	0.6	5	4	1.0
Millwoods	320	0.1	0.5	1	1	0.9
Thorncliff	290	0.1	0.6	1	10	0.9
Ormsby	300	0.1	0.6	1	5	0.9
Burnewood	270	0.1	0.5	1	1	0.9
Londonderry	260	0.1	0.6	1	2	0.9

* Original sample diluted x10 prior to analysis.

Note All Aluminium values were obtained after a ten fold dilution of the original sample prior to analysis.

Reservoir Metals Data (March 1989)

Reservoir	Aluminium (ppb)	Cadmium (ppb)	Chromium (ppb)	Copper (ppb)	Iron (ppb)	Lead (ppb)
Clareview	290	0.1	0.5	3	2	0.6
Papaschase # 1	330	0.1	0.5	1	60 *	0.6
Papaschase # 2	300	0.1	0.7	1	3	0.8
Kaskitayo	290	0.2	0.6	0	3	0.6
Castledowns	340	0.1	0.7	1	2	0.9
North Jasper	310	0.1	0.6	1	2	0.7
Rosslyn # 1	300	0.1	0.6	2	7	0.8
Rosslyn # 2	300	0.1	0.6	1	40 *	0.8
Millwoods	300	0.1	0.6	1	1	0.8
Thorncliff	360	0.1	0.7	1	3	0.9
Ormsby	300	0.1	0.6	0	2	0.8
Burnewood	290	0.1	0.6	1	1	0.9
Londonderry	310	0.1	0.6	1	2	0.8

* Original sample diluted x10 prior to analysis.

Note All Aluminium values were obtained after a ten fold dilution of the original sample prior to analysis.

Reservoir Metals Data (April 1989)

Reservoir	Aluminium	Cadmium	Chromium	Copper	Iron	Lead
	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)
Clareview	310	0.2	0.3	2	20	0.5
Papaschase # 1	550	0.2	0.6	2	40 *	0.7
Papaschase # 2	480	0.2	0.5	3	10	0.7
Kaskitayo	330	0.2	0.3	1	16	0.7
Castledowns	240	0.2	0.7	1	1	0.8
North Jasper	280	0.2	0.5	2	1	0.6
Rosslyn # 1	290	0.2	0.5	2	4	0.6
Rosslyn # 2	250	0.2	0.4	1	11	0.6
Millwoods	320	0.2	0.3	2	6	0.7
Thorncliff	300	0.2	0.4	2	22	0.7
Ormsby	350	0.2	0.4	1	13	0.8
Burnewood	390	0.2	0.5	1	6	0.7
Londonderry	260	0.2	0.6	1	2	0.8

* Original sample diluted x10 prior to analysis.

Note All Aluminium values were obtained after a ten fold dilution of the original sample prior to analysis.

Fire Hall Non Metals Data (May 1988)

Fire Hall	Total Chloramines	Total Oxidants	Fluoride Ion	pH	Turbidity	Total Hardness	Calcium Hardness	Total Alkalinity	Organic Carbon
	(ppm)	(ppm)	(ppm)		(NTU)	(ppm)	(ppm)	(ppm)	(HAU)
# 1	1.97	0.27	1.07	8.2	0.10	107	61	55	3.4
# 2	2.03	0.33	1.03	8.2	0.05	104	61	56	3.3
# 3	2.01	0.30	1.01	8.2	0.10	118	70	63	2.7
# 4	1.98	0.29	0.96	8.1	0.15	110	70	51	2.0
# 5	2.08	0.42	0.99	8.1	0.40	123	74	66	3.1
# 6	1.91	0.36	0.99	8.2	0.25	131	76	76	3.0
# 7	2.03	0.40	1.01	8.1	0.20	124	74	65	2.9
# 8	1.99	0.26	0.98	8.2	0.10	118	69	52	2.2
# 9	1.85	0.24	1.02	8.2	0.20	124	70	62	2.3
# 10	2.05	0.40	1.01	8.1	0.10	125	74	67	3.0
# 11 **									
# 12	1.94	0.20	0.94	8.2	0.10	126	76	54	2.9
# 13	1.88	0.24	1.06	8.2	0.10	119	70	49	2.3
# 15	1.92	0.28	1.01	8.2	0.10	120	72	66	2.8
# 16	2.02	0.21	1.03	8.2	0.10	124	69	50	1.9
# 17	1.88	0.34	0.99	8.2	0.20	110	70	49	2.0
# 19	1.92	0.26	0.98	8.2	0.10	124	69	46	2.5
# 20	2.01	0.18	1.00	8.2	0.10	119	69	52	2.4
# 22	2.00	0.31	1.10	8.2	0.05	105	61	47	3.3
# 23 **									
# 24 **									

** No samples were collected from Fire Halls #11, #23, and #24 during the month of May.

Fire Hall Non Metals Data (June 1988)

Fire Hall	Total Chloramines	Total Oxidants	Fluoride Ion	pH	Turbidity	Total Hardness	Calcium Hardness	Total Alkalinity	Organic Carbon
	(ppm)	(ppm)	(ppm)		(NTU)	(ppm)	(ppm)	(ppm)	(HAU)
# 1	1.90	0.26	1.04	8.0	0.05	110	61	48	2.7
# 2	2.00	0.24	1.02	8.0	0.05	115	63	47	2.8
# 3	1.81	0.23	1.04	8.2	0.10	110	65	48	2.1
# 4	1.75	0.27	1.00	8.2	0.05	115	69	48	4.7
# 5 **									
# 6	1.80	0.19	1.01	8.1	0.10	112	65	45	2.6
# 7	1.75	0.21	0.97	8.1	0.10	114	65	55	3.0
# 8 **									
# 9	1.81	0.19	1.03	8.1	0.05	110	66	44	2.3
# 10	1.99	0.30	0.97	8.1	0.20	117	66	58	2.6
# 11	1.96	0.21	0.97	8.2	0.10	110	59	56	2.0
# 12	1.88	0.23	1.05	8.2	0.10	115	68	51	2.1
# 13	1.90	0.24	1.05	8.2	0.10	110	67	45	2.3
# 15	1.78	0.17	1.02	8.1	0.10	112	69	45	2.2
# 16	1.81	0.23	1.04	8.2	0.05	112	67	46	1.8
# 17	2.02	0.19	1.06	8.1	0.10	111	62	46	2.5
# 19 **									
# 20	1.97	0.21	1.02	8.2	0.10	108	64	45	1.5
# 22	1.79	0.24	1.02	8.3	0.05	113	70	53	2.8
# 23	2.03	0.23	1.01	8.2	0.10	116	68	46	2.2
# 24	1.92	0.23	0.97	8.2	0.20	119	67	61	2.2

** No samples were collected from Fire Halls #5, #8, and #19 during the month of June.

Fire Hall Non Metals Data (July 1988)

Fire Hall	Total Chloramines	Total Oxidants	Fluoride Ion	pH	Turbidity	Total Hardness	Calcium Hardness	Total Alkalinity	Organic Carbon
	(ppm)	(ppm)	(ppm)		(NTU)	(ppm)	(ppm)	(ppm)	(HAU)
# 1	1.92	0.36	1.06	8.3	0.35	121	81	40	4.4
# 2	2.01	0.36	1.03	8.3	0.35	122	80	38	4.7
# 3	1.90	0.25	1.01	8.3	0.20	118	77	43	3.2
# 4	2.00	0.24	1.04	8.3	0.10	119	80	46	3.9
# 5	2.03	0.36	1.04	8.2	0.10	120	77	47	4.8
# 6	1.92	0.33	0.95	8.4	0.15	114	69	42	3.6
# 7	2.03	0.25	0.99	8.0	0.10	115	68	49	2.8
# 8	1.94	0.27	1.04	8.4	0.10	120	80	46	4.9
# 9	1.95	0.21	0.98	8.2	0.10	118	75	42	3.2
# 10	1.96	0.30	1.03	8.3	0.10	118	75	46	5.0
# 11	2.10	0.29	0.94	8.4	0.25	117	70	43	4.0
# 12	2.01	0.32	0.99	8.3	0.20	119	79	42	3.1
# 13	1.96	0.34	1.00	8.3	0.20	117	79	42	3.2
# 15	1.90	0.37	0.99	8.3	0.10	111	73	39	3.2
# 16	2.01	0.25	0.97	8.3	0.15	119	70	39	3.3
# 17	1.92	0.30	0.97	8.3	0.20	120	79	46	4.4
# 19	1.98	0.32	1.03	8.3	0.10	118	75	39	2.8
# 20	1.97	0.27	0.98	8.3	0.20	117	75	42	3.3
# 22	2.00	0.30	1.01	8.2	0.10	118	66	48	3.2
# 23	1.90	0.31	0.99	8.4	0.10	111	73	47	2.3
# 24	2.01	0.25	0.98	8.3	0.50	119	76	46	4.6

Fire Hall Non Metals Data (September 1988)

Fire Hall	Total Chloramines (ppm)	Total Oxidants (ppm)	Fluoride Ion (ppm)	pH	Turbidity (NTU)	Total Hardness (ppm)	Calcium Hardness (ppm)	Total Alkalinity (ppm)	Organic Carbon (HAU)
# 1	1.89	0.27	1.02	8.3	1.00	112	63	62	2.6
# 2	1.99	0.30	1.01	8.3	0.90	110	64	63	2.8
# 3	1.80	0.29	0.98	8.4	0.10	112	61	53	2.1
# 4	1.91	0.26	1.04	8.4	0.10	112	71	55	2.9
# 5	1.82	0.31	1.03	8.2	0.45	111	68	59	2.8
# 6	1.90	0.19	0.99	8.3	0.50	112	65	58	2.5
# 7	1.96	0.26	0.95	8.4	0.70	112	77	68	3.3
# 8	1.84	0.34	0.99	8.4	0.25	114	69	57	3.8
# 9	1.86	0.34	0.99	8.3	0.30	110	72	53	1.9
# 10	1.75	0.30	0.96	8.2	0.40	112	68	58	2.8
# 11	1.89	0.30	0.92	8.3	0.35	111	75	73	3.4
# 12	1.79	0.33	0.96	8.4	0.40	112	74	59	2.8
# 13	1.93	0.29	0.98	8.3	0.25	111	70	57	2.5
# 15	1.88	0.25	1.02	8.4	0.20	109	67	55	2.1
# 16	1.85	0.29	0.96	8.5	0.10	111	66	60	2.2
# 17	1.82	0.30	0.99	8.3	0.30	109	74	53	3.1
# 19	1.80	0.24	1.02	8.4	0.10	112	69	59	2.2
# 20	1.94	0.21	1.04	8.4	0.10	112	70	51	2.8
# 22	1.82	0.33	1.00	8.3	1.30	111	68	63	2.7
# 23	1.88	0.28	0.99	8.5	0.30	111	70	52	2.7
# 24	1.95	0.33	1.01	8.2	0.40	114	70	61	3.8

Fire Hall Non Metals Data (October 1988)

Fire Hall	Total Chloramines	Total Oxidants	Fluoride Ion	pH	Turbidity	Total Hardness	Calcium Hardness	Total Alkalinity	Organic Carbon
	(ppm)	(ppm)	(ppm)		(NTU)	(ppm)	(ppm)	(ppm)	(HAU)
# 1	2.01	0.37	0.97	8.3	0.30	120	69	67	2.8
# 2	2.06	0.32	0.97	8.3	0.25	117	70	66	2.9
# 3	1.91	0.32	1.03	8.4	0.25	112	70	59	1.7
# 4	1.97	0.35	0.97	8.6	0.15	108	70	55	1.4
# 5	2.02	0.37	0.96	8.2	0.35	118	69	65	2.3
# 6	2.01	0.30	0.99	8.3	0.20	120	74	66	1.9
# 7	1.96	0.35	1.08	8.3	0.25	118	71	69	1.9
# 8	2.01	0.34	0.94	8.4	0.25	116	68	57	3.0
# 9	1.81	0.34	0.98	8.4	0.30	111	70	59	2.1
# 10	1.91	0.26	1.03	8.4	0.20	118	69	64	2.1
# 11	1.92	0.21	0.96	8.3	0.25	120	76	71	2.5
# 12	2.01	0.37	1.02	8.3	0.35	109	70	61	1.8
# 13	1.98	0.27	0.99	8.4	0.20	109	69	53	1.6
# 15	1.99	0.28	0.97	8.5	0.15	111	67	54	1.8
# 16	1.95	0.26	1.06	8.5	0.25	111	71	58	2.2
# 17	1.98	0.34	1.05	8.5	0.15	112	72	57	2.0
# 19	1.94	0.32	0.99	8.3	0.15	117	70	59	1.8
# 20	1.99	0.33	0.97	8.4	0.05	116	72	58	1.8
# 22	2.03	0.31	1.00	8.2	0.40	119	69	69	3.4
# 23	1.93	0.29	0.98	8.3	0.30	111	70	57	1.6
# 24	2.02	0.28	0.98	8.3	0.30	115	70	69	2.6

Fire Hall Non Metals Data (November 1988)

Fire Hall	Total Chloramines	Total Oxidants	Fluoride Ion	pH	Turbidity	Total Hardness	Calcium Hardness	Total Alkalinity	Organic Carbon
	(ppm)	(ppm)	(ppm)		(NTU)	(ppm)	(ppm)	(ppm)	(HAU)
# 1	2.05	0.28	1.00	8.3	0.25	104	58	50	3.4
# 2	2.00	0.29	1.04	8.3	0.20	105	54	51	3.5
# 3	2.00	0.23	1.03	8.3	0.25	109	66	48	2.5
# 4	2.06	0.21	1.02	8.5	0.10	110	62	47	2.1
# 5	1.98	0.36	0.99	8.3	0.15	107	56	49	3.6
# 6	2.00	0.33	1.01	8.2	0.20	121	66	63	2.4
# 7	1.98	0.25	1.00	8.4	0.25	110	61	59	2.5
# 8	1.99	0.32	1.01	8.3	0.20	110	59	60	2.7
# 9	1.93	0.27	1.02	8.2	0.20	110	63	47	1.8
# 10	2.01	0.24	0.99	8.3	0.40	112	67	61	2.7
# 11	1.97	0.27	0.97	8.3	0.35	111	61	67	3.1
# 12	1.94	0.27	1.02	8.4	0.30	115	64	47	2.3
# 13	1.98	0.25	1.05	8.4	0.20	110	63	50	2.4
# 15	1.95	0.23	1.01	8.2	0.35	109	64	48	1.9
# 16	2.00	0.24	0.96	8.4	0.60	105	63	47	2.4
# 17	1.97	0.26	1.00	8.5	0.20	107	63	49	2.2
# 19	2.00	0.24	1.01	8.3	0.20	108	62	49	1.9
# 20	2.00	0.25	1.02	8.3	0.15	108	61	47	2.4
# 22	1.96	0.26	0.98	8.3	0.30	103	53	48	3.2
# 23	2.14	0.24	0.98	8.4	0.25	104	62	48	2.2
# 24	1.95	0.27	1.03	8.3	0.35	110	59	61	2.7

Fire Hall Non Metals Data (December 1988)

Fire Hall	Total Chloramines	Total Oxidants	Fluoride Ion	pH	Turbidity	Total Hardness	Calcium Hardness	Total Alkalinity	Organic Carbon
	(ppm)	(ppm)	(ppm)		(NTU)	(ppm)	(ppm)	(ppm)	(HAU)
# 1	2.06	0.32	1.00	8.4	0.25	104	53	50	2.5
# 2	1.99	0.29	1.02	8.4	0.25	106	56	50	2.1
# 3	1.94	0.24	0.95	8.5	0.40	113	62	54	2.0
# 4	1.90	0.27	0.96	8.3	0.70	105	66	46	1.2
# 5	2.05	0.32	0.96	8.4	0.35	106	60	48	2.2
# 6	1.91	0.27	0.96	8.4	0.35	112	61	57	2.5
# 7	1.84	0.28	1.01	8.4	0.25	111	56	54	1.2
# 8	1.90	0.27	1.00	8.4	0.55	109	62	47	1.3
# 9	1.89	0.26	0.98	8.5	0.40	109	62	51	3.0
# 10	1.92	0.29	1.00	8.3	0.35	109	58	53	1.4
# 11	1.97	0.29	0.99	8.3	0.45	108	56	54	1.2
# 12	1.98	0.28	0.95	8.5	0.35	107	60	52	1.8
# 13	1.84	0.29	0.98	8.5	0.40	106	58	52	2.2
# 15	1.87	0.31	0.99	8.4	0.45	108	61	54	2.5
# 16	1.86	0.31	0.98	8.5	0.45	106	61	50	2.2
# 17	1.90	0.28	0.98	8.4	0.35	108	64	46	1.9
# 19	1.97	0.27	1.02	8.5	0.35	106	59	54	1.9
# 20	1.90	0.29	1.02	8.4	0.35	108	62	56	1.9
# 22	2.06	0.31	0.99	8.3	0.45	107	56	50	2.3
# 23	2.01	0.26	0.98	8.4	0.55	107	64	48	1.3
# 24	1.87	0.27	1.00	8.5	0.30	113	60	59	2.3

Fire Hall Non Metals Data (January 1989)

Fire Hall	Total Chloramines	Total Oxidants	Fluoride Ion	pH	Turbidity	Total Hardness	Calcium Hardness	Total Alkalinity	Organic Carbon
	(ppm)	(ppm)	(ppm)		(NTU)	(ppm)	(ppm)	(ppm)	(HAU)
# 1	1.97	0.31	0.99	8.4	0.40	115	60	64	3.7
# 2	1.99	0.30	0.97	8.4	0.15	114	60	60	4.0
# 3	1.94	0.26	0.99	8.5	0.30	116	65	56	4.1
# 4	1.94	0.26	1.02	8.4	0.20	109	63	56	3.1
# 5	1.98	0.31	0.94	8.3	0.15	117	62	62	3.8
# 6	1.87	0.25	1.03	8.4	0.50	115	64	60	3.3
# 7	1.97	0.27	0.97	8.4	0.15	111	55	54	4.8
# 8	1.90	0.24	1.00	8.4	0.25	110	64	55	2.9
# 9	1.84	0.27	0.98	8.4	0.20	112	66	56	3.2
# 10	1.92	0.26	0.96	8.3	0.50	110	59	57	3.2
# 11	1.96	0.27	0.98	8.4	0.25	113	60	56	4.0
# 12	1.95	0.27	0.95	8.4	0.15	111	63	55	2.9
# 13	1.88	0.27	1.02	8.4	0.40	109	61	54	3.1
# 15	1.90	0.28	1.00	8.5	0.30	115	63	55	3.4
# 16	1.88	0.29	1.01	8.5	0.15	111	63	52	2.7
# 17	1.87	0.27	0.96	8.5	0.25	112	63	58	2.7
# 19	1.94	0.27	0.97	8.4	0.20	115	61	54	3.5
# 20	1.95	0.25	1.03	8.4	0.25	112	63	53	3.4
# 22	1.99	0.30	0.96	8.4	0.20	111	56	55	4.7
# 23	1.91	0.29	0.99	8.4	0.50	110	63	59	2.5
# 24	2.00	0.25	0.99	8.4	0.25	114	55	54	3.9

Fire Hall Non Metals Data (February 1989)

Fire Hall	Total Chloramines	Total Oxidants	Fluoride Ion	pH	Turbidity	Total Hardness	Calcium Hardness	Total Alkalinity	Organic Carbon
	(ppm)	(ppm)	(ppm)		(NTU)	(ppm)	(ppm)	(ppm)	(HAU)
# 1	2.03	0.29	1.04	8.3	0.10	119	61	63	4.1
# 2	2.04	0.27	1.02	8.4	0.10	118	64	62	3.1
# 3	1.92	0.29	1.02	8.4	0.10	115	68	56	4.6
# 4	1.93	0.27	0.97	8.3	0.10	119	67	54	3.7
# 5	2.02	0.32	1.01	8.3	0.10	114	59	55	3.5
# 6	1.91	0.29	1.01	8.4	0.15	114	66	51	3.5
# 7	1.97	0.24	0.98	8.3	0.05	119	63	58	3.7
# 8	1.90	0.27	0.98	8.4	0.10	111	68	51	3.1
# 9	1.90	0.31	1.04	8.5	0.10	119	65	60	3.9
# 10	1.97	0.25	0.98	8.3	0.10	114	62	58	3.4
# 11	1.95	0.26	1.00	8.4	0.05	115	60	57	3.7
# 12	1.90	0.28	1.00	8.4	0.25	113	64	55	3.1
# 13	1.92	0.32	0.99	8.4	0.15	113	64	54	3.3
# 15	1.90	0.32	1.00	8.5	0.10	113	64	49	3.3
# 16	1.95	0.32	0.99	8.5	0.10	114	65	50	3.7
# 17	1.90	0.31	1.00	8.5	0.10	115	66	49	2.8
# 19	1.93	0.31	0.99	8.4	0.15	114	66	49	2.7
# 20	1.96	0.30	0.99	8.5	0.15	115	67	48	3.1
# 22	2.05	0.27	0.97	8.4	0.15	118	64	63	3.5
# 23	1.95	0.31	0.97	8.4	0.10	115	67	52	3.5
# 24	1.98	0.29	0.99	8.4	0.10	116	61	61	3.6

Fire Hall Non Metals Data (March 1989)

Fire Hall	Total Chloramines	Total Oxidants	Fluoride Ion	pH	Turbidity	Total Hardness	Calcium Hardness	Total Alkalinity	Organic Carbon
	(ppm)	(ppm)	(ppm)		(NTU)	(ppm)	(ppm)	(ppm)	(HAU)
# 1	1.94	0.32	0.99	8.4	0.10	114	60	56	4.4
# 2	1.96	0.31	0.97	8.4	0.10	116	63	60	4.4
# 3	1.95	0.30	0.97	8.5	0.10	118	62	60	3.7
# 4	1.94	0.34	0.90	8.5	0.05	110	70	43	2.9
# 5	1.93	0.33	0.96	8.3	0.10	114	59	57	4.4
# 6	1.94	0.32	0.96	8.2	0.20	116	68	48	3.0
# 7	1.91	0.27	1.02	8.3	0.15	116	63	58	4.4
# 8	1.95	0.29	0.94	8.5	0.10	117	71	47	3.8
# 9	1.95	0.27	0.97	8.4	0.10	115	69	43	3.2
# 10	1.90	0.26	0.94	8.3	0.10	117	62	53	3.8
# 11	1.98	0.26	0.96	8.3	0.15	115	62	51	4.3
# 12	1.91	0.28	1.01	8.3	0.05	113	69	42	3.1
# 13	1.97	0.28	1.00	8.4	0.10	114	68	44	3.1
# 15	1.97	0.29	0.95	8.4	0.10	116	71	42	3.5
# 16	1.94	0.27	0.96	8.4	0.10	111	68	40	3.6
# 17	1.97	0.30	0.97	8.6	0.10	111	71	45	3.1
# 19	2.01	0.30	1.00	8.3	0.10	112	68	42	3.2
# 20	1.97	0.33	1.02	8.3	0.05	118	72	43	3.1
# 22	1.94	0.32	0.99	8.3	0.10	114	59	55	4.5
# 23	1.91	0.31	0.93	8.6	0.10	115	68	47	3.1
# 24	1.95	0.30	0.97	8.5	0.10	111	61	54	4.8

Fire Hall Non Metals Data (April 1989)

Fire Hall	Total Chloramines	Total Oxidants	Fluoride Ion	pH	Turbidity	Total Hardness	Calcium Hardness	Total Alkalinity	Organic Carbon
	(ppm)	(ppm)	(ppm)		(NTU)	(ppm)	(ppm)	(ppm)	(HAU)
# 1	2.00	0.31	1.00	8.3	0.15	108	68	44	5.2
# 2	2.02	0.30	0.99	8.3	0.10	109	69	43	5.1
# 3	1.90	0.29	0.98	8.5	0.20	106	74	46	10.8
# 4	1.85	0.30	1.03	8.3	0.10	109	77	40	7.3
# 5	1.93	0.34	0.94	8.2	0.20	113	80	50	6.0
# 6	1.89	0.27	1.01	8.5	0.15	104	73	43	10.9
# 7	1.97	0.30	0.93	8.2	0.15	116	84	51	6.9
# 8	1.95	0.31	0.97	8.0	0.20	113	78	53	6.8
# 9	1.86	0.30	0.99	8.4	0.20	112	75	44	10.4
# 10	1.90	0.31	0.93	8.2	0.25	117	79	46	7.0
# 11	2.00	0.29	0.92	8.2	0.15	118	80	50	6.1
# 12	1.86	0.29	1.00	8.4	0.15	110	75	45	10.6
# 13	1.93	0.26	0.99	8.5	0.15	107	73	48	11.0
# 15	1.91	0.28	0.97	8.3	0.10	105	74	47	10.7
# 16	1.87	0.30	1.01	8.5	0.15	108	76	40	10.1
# 17	1.99	0.25	0.96	8.2	0.15	112	79	46	6.7
# 19	1.86	0.27	1.01	8.4	0.15	112	79	43	10.8
# 20	1.90	0.28	0.99	8.4	0.10	108	72	46	10.9
# 22	1.93	0.30	0.99	8.0	0.10	108	72	51	6.5
# 23	1.84	0.31	0.99	8.1	0.10	106	74	41	5.7
# 24	1.97	0.33	0.91	8.2	0.15	121	82	51	6.4

Fire Hall Metals Data (July 1988)

Fire Hall	Aluminium (ppb)	Cadmium (ppb)	Chromium (ppb)	Copper (ppb)	Iron (ppb)	Lead (ppb)
# 1	260	0.1	0.5	1	4	1.0
# 2	260	0.1	0.5	1	5	0.9
# 3	260	0.1	0.6	1	13	0.9
# 4	300	0.1	0.5	1	10	1.4
# 5	260	0.2	0.6	2	12	0.8
# 6	350	0.1	0.6	2	14	1.2
# 7	300	0.1	0.6	1	3	0.9
# 8	290	0.1	0.5	2	6	1.0
# 9	270	0.1	0.5	1	7	0.9
# 10	210	0.4	0.4	2	20	0.9
# 11	240	0.1	0.5	1	9	1.0
# 12	250	0.1	0.4	1	13	1.0
# 13	310	0.1	0.5	1	18	1.0
# 15	290	0.1	0.7	3	19	1.0
# 16	290	0.1	0.6	1	4	1.1
# 17	300	0.1	0.6	2	8	1.0
# 19	290	0.1	0.6	2	11	0.9
# 20	300	0.1	0.7	1	5	1.0
# 22	260	0.1	0.5	1	4	1.1
# 23	240	0.1	0.6	4	2	1.4
# 24	240	0.1	0.4	1	4	0.9

Note All Aluminium values were obtained after a ten fold dilution of the original sample prior to analysis.

Fire Hall Metals Data (September 1988)

Fire Hall	Aluminium	Cadmium	Chromium	Copper	Iron	Lead
	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)
# 1	390	0.1	0.6	2	6	0.8
# 2	380	0.2	0.7	1	4	0.9
# 3	350	0.1	0.6	1	7	0.7
# 4	400	0.1	0.7	3	3	0.7
# 5	360	0.1	0.6	4	6	0.8
# 6	360	0.2	0.4	2	2	0.9
# 7	350	0.1	0.5	2	4	0.8
# 8	340	0.2	0.6	3	11	0.9
# 9	300	0.1	0.7	5	12	1.0
# 10	320	0.1	0.8	2	3	0.7
# 11	380	0.1	0.6	1	5	0.9
# 12	420	0.1	0.5	3	3	0.7
# 13	410	0.2	0.7	1	9	0.9
# 15	240	0.1	0.6	2	3	0.8
# 16	290	0.1	0.5	2	3	1.0
# 17	300	0.2	0.4	3	4	0.8
# 19	350	0.1	0.5	1	5	0.8
# 20	380	0.2	0.6	6	3	0.7
# 22	360	0.2	0.5	1	2	0.9
# 23	310	0.1	0.7	2	8	0.8
# 24	330	0.1	0.6	1	4	0.9

Note All Aluminium values were obtained after a ten fold dilution of the original sample prior to analysis.

Fire Hall Metals Data (October 1988)

Fire Hall	Aluminium (ppb)	Cadmium (ppb)	Chromium (ppb)	Copper (ppb)	Iron (ppb)	Lead (ppb)
# 1	490	0.1	0.5	2	5	0.5
# 2	420	0.1	0.5	1	5	0.6
# 3	330	0.2	0.6	14	10	1.6
# 4	300	0.2	0.5	30 **	8	0.8
# 5	440	0.2	0.6	7	12	0.5
# 6	370	0.2	0.7	12	9	0.8
# 7	390	0.1	0.3	2	3	0.7
# 8	370	0.2	0.5	5	40 *	0.9
# 9	390	0.2	0.7	9	12	0.7
# 10	380	0.1	0.4	5	4	12.8
# 11	370	0.1	0.5	6	8	0.6
# 12	330	0.2	0.5	5	5	0.7
# 13	270	0.2	0.6	2	15	0.8
# 15	290	0.2	0.6	6	8	9.9
# 16	350	0.2	0.6	16	5	1.0
# 17	400	0.1	0.5	3	4	1.2
# 19	260	0.2	0.5	5	5	0.9
# 20	270	0.2	0.6	8	10	0.8
# 22	300	0.2	0.4	5	4	0.6
# 23	295	0.6	0.6	7	5	1.0
# 24	450	0.1	0.8	4	6	0.8

* Original sample diluted x10 prior to analysis.

Note All Aluminium values were obtained after a ten fold dilution of the original sample prior to analysis.

Fire Hall Metals Data (November 1988)

Fire Hall	Aluminium (ppb)	Cadmium (ppb)	Chromium (ppb)	Copper (ppb)	Iron (ppb)	Lead (ppb)
# 1	350	0.2	0.5	3	4	1.1
# 2	370	0.2	0.6	2	2	3.0
# 3	410	0.3	0.8	4	17	0.7
# 4	550	0.4	0.6	1	5	0.6
# 5	340	0.2	0.5	2	2	1.1
# 6	340	0.3	0.5	1	2	0.9
# 7	370	0.2	0.6	2	10	0.6
# 8	390	0.1	0.5	2	7	0.6
# 9	410	0.3	0.6	2	9	0.9
# 10	400	0.4	0.5	1	7	0.5
# 11	350	0.1	0.5	1	9	0.7
# 12	360	0.3	0.6	1	7	0.8
# 13	370	0.3	0.6	4	12	0.8
# 15	380	0.2	0.6	5	5	1.1
# 16	390	0.3	0.6	6	7	1.0
# 17	510	0.3	0.6	2	4	0.7
# 19	400	0.3	0.6	2	4	0.8
# 20	410	0.3	0.5	2	3	1.3
# 22	340	0.2	0.6	2	3	0.7
# 23	560	0.3	0.6	8	4	0.6
# 24	370	0.1	0.6	1	3	0.6

Note All Aluminium values were obtained after a ten fold dilution of the original sample prior to analysis.

Fire Hall Metals Data (December 1988)

Fire Hall	Aluminium (ppb)	Cadmium (ppb)	Chromium (ppb)	Copper (ppb)	Iron (ppb)	Lead (ppb)
# 1	350	0.2	0.4	1	4	0.8
# 2	330	0.2	0.5	0	3	0.8
# 3	320	0.1	0.7	1	9	1.0
# 4	460	0.1	0.4	1	7	0.8
# 5	360	0.2	0.5	1	7	0.8
# 6	360	0.2	0.4	10	12	1.1
# 7	340	0.1	0.3	1	3	0.8
# 8	380	0.1	0.3	2	13	0.8
# 9	490	0.1	0.4	3	11	0.8
# 10	360	0.1	0.3	2	3	0.8
# 11	340	0.1	0.3	1	14	0.8
# 12	390	0.1	0.3	4	4	1.4
# 13	380	0.1	0.4	1	12	0.9
# 15	300	0.1	0.5	1	2	1.0
# 16	460	0.1	0.5	3	3	0.8
# 17	440	0.2	0.4	3	7	0.9
# 19	380	0.1	0.5	2	5	0.8
# 20	330	0.1	0.5	3	3	0.8
# 22	470	0.1	0.4	1	3	1.0
# 23	460	0.1	0.4	3	3	0.8
# 24	290	0.2	0.5	1	5	0.8

Note. All Aluminium values were obtained after a ten fold dilution of the original sample prior to analysis.

Fire Hall Metals Data (January 1989)

Fire Hall	Aluminium	Cadmium	Chromium	Copper	Iron	Lead
	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)
# 1	400	0.1	0.6	1	1	1.1
# 2	400	0.1	0.6	2	1	1.2
# 3	450	0.2	0.7	2	5	1.3
# 4	460	0.2	0.6	3	2	1.2
# 5	420	0.1	0.6	2	1	1.2
# 6	440	0.1	0.7	6	8	1.3
# 7	430	0.2	0.5	2	1	1.2
# 8	430	0.2	0.6	3	5	1.2
# 9	430	0.2	0.7	4	2	1.2
# 10	430	0.2	0.6	1	3	1.2
# 11	450	0.2	0.6	3	4	1.2
# 12	420	0.2	0.7	2	1	1.1
# 13	430	0.2	0.7	2	3	1.2
# 15	440	0.2	0.7	3	2	1.2
# 16	420	0 1	0.7	2	1	1.1
# 17	420	0.2	0.6	3	3	1.2
# 19	410	0.1	0.7	3	3	1.2
# 20	420	0.1	0.7	3	1	1.1
# 22	480	0.2	0.4	6	8	1.5
# 23	490	0.3	0.6	9	3	1.3
# 24	540	0.2	0.5	1	2	1.3

Note All Aluminium values were obtained after a ten fold dilution of the original sample prior to analysis.

Fire Hall Metals Data (February 1989)

Fire Hall	Aluminium	Cadmium	Chromium	Copper	Iron	Lead
	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)
# 1	240	0.1	0.6	1	1	0.8
# 2	240	0.1	0.6	1	1	0.9
# 3	300	0.1	0.8	1	5	1.0
# 4	320	0.1	0.7	3	1	1.0
# 5	260	0.1	0.6	3	2	0.8
# 6	280	0.1	0.7	5	6	1.0
# 7	250	0.1	0.6	2	2	0.7
# 8	300	0.1	0.6	3	6	0.9
# 9	280	0.1	0.7	3	4	0.9
# 10	290	0.1	0.9	1	3	0.8
# 11	240	0.1	0.7	7	2	0.8
# 12	270	0.1	0.7	2	2	1.1
# 13	300	0.1	0.8	2	3	0.8
# 15	300	0.2	0.8	3	1	0.9
# 16	300	0.1	0.8	3	2	1.0
# 17	300	0.1	0.8	3	3	0.9
# 19	300	0.1	0.8	3	4	1.1
# 20	300	0.1	0.8	3	2	0.9
# 22	250	0.1	0.8	1	1	0.9
# 23	310	0.2	0.7	4	1	1.0
# 24	250	0.1	0.7	1	1	0.8

Note All Aluminium values were obtained after a ten fold dilution of the original sample prior to analysis.

Fire Hall Metals Data (March 1989)

Fire Hall	Aluminium (ppb)	Cadmium (ppb)	Chromium (ppb)	Copper (ppb)	Iron (ppb)	Lead (ppb)
# 1	280	0.1	0.5	1	1	0.4
# 2	280	0.1	0.5	1	1	0.3
# 3	290	0.1	0.7	2	2	0.8
# 4	280	0.2	0.6	2	1	0.7
# 5	290	0.1	0.5	2	2	0.3
# 6	280	0.1	0.6	2	1	1.2
# 7	260	0.1	0.5	2	1	0.3
# 8	290	0.1	0.6	2	2	0.6
# 9	320	0.2	0.6	8	2	0.8
# 10	300	0.1	0.5	2	1	0.5
# 11	280	0.1	0.5	2	1	0.6
# 12	280	0.1	0.7	4	1	0.8
# 13	280	0.1	0.7	1	4	0.8
# 15	280	0.2	0.7	5	1	1.2
# 16	310	0.1	0.7	5	1	0.8
# 17	310	0.1	0.6	2	1	0.7
# 19	290	0.1	0.7	1	1	0.8
# 20	280	0.1	0.6	2	1	0.9
# 22	260	0.1	0.5	1	1	0.4
# 23	270	0.1	0.6	4	1	0.7
# 24	260	0.2	0.5	2	1	0.3

Note All Aluminium values were obtained after a ten fold dilution of the original sample prior to analysis.

Fire Hall Metals Data (April 1989)

Fire Hall	Aluminium (ppb)	Cadmium (ppb)	Chromium (ppb)	Copper (ppb)	Iron (ppb)	Lead (ppb)
# 1	310	0.2	0.6	4	40 *	1.0
# 2	320	0.2	0.6	4	40 *	0.8
# 3	340	0.2	0.5	12	40 *	0.7
# 4	350	0.3	0.5	10	40 *	0.9
# 5	400	0.3	0.5	3	19	0.8
# 6	330	0.2	0.4	7	8	0.6
# 7	310	0.3	0.5	4	19	0.8
# 8	240	0.2	0.4	4	40 *	0.8
# 9	490	0.2	0.4	6	14	0.7
# 10	320	0.2	0.5	2	16	0.8
# 11	330	0.2	0.5	4	17	0.9
# 12	440	0.2	0.5	18	21	0.9
# 13	300	0.2	0.3	3	17	0.6
# 15	310	0.2	0.5	10	12	0.7
# 16	350	0.2	0.5	11	11	0.8
# 17	330	0.3	0.7	9	15	0.9
# 19	310	0.3	0.5	6	20	0.7
# 20	360	0.2	0.7	16	11	0.7
# 22	360	0.2	0.4	2	13	0.8
# 23	240	0.2	0.5	9	10	0.8
# 24	470	0.3	0.5	3	14	0.8

* Original sample diluted x10 prior to analysis.

Note All Aluminium values were obtained after a ten fold dilution of the original sample prior to analysis.

Total Chloramines

Units; ppm (mg/L) as Chlorine (Cl_2)

Month	Rossdale Reservoirs	Smith Reservoirs	Rossdale Fire halls	Smith Fire Halls
	(ppm as Cl_2)	(ppm as Cl_2)	(ppm as Cl_2)	(ppm as Cl_2)
May	1.98 ± 0.06	2.04 ± 0.04	2.00 ± 0.05	1.93 ± 0.05
June	1.98 ± 0.04	1.97 ± 0.06	1.86 ± 0.10	1.96 ± 0.07
July	1.94 ± 0.05	1.98 ± 0.06	1.98 ± 0.06	1.96 ± 0.04
August	1.82 ± 0.08	1.84 ± 0.05	*	
September	1.81 ± 0.06	1.96 ± 0.08	1.88 ± 0.07	1.86 ± 0.07
October	1.97 ± 0.05	1.96 ± 0.03	1.99 ± 0.05	1.97 ± 0.03
November	1.96 ± 0.07	1.98 ± 0.04	1.99 ± 0.04	1.99 ± 0.03
December	1.92 ± 0.06	1.94 ± 0.04	1.95 ± 0.08	1.93 ± 0.06
January	1.93 ± 0.05	1.96 ± 0.01	1.95 ± 0.04	1.92 ± 0.04
February	1.95 ± 0.02	1.96 ± 0.04	1.97 ± 0.05	1.93 ± 0.03
March	1.97 ± 0.09	1.98 ± 0.03	1.94 ± 0.02	1.96 ± 0.04
April	1.86 ± 0.04	1.93 ± 0.04	1.94 ± 0.05	1.90 ± 0.06

* No samples were collected from the fire halls in August.

Total Oxidants

Units; ppm (mg/L) as Chlorite (ClO_2^-)

Month	Rossdale Reservoirs	Smith Reservoirs	Rossdale Fire halls	Smith Fire Halls
	(ppm as ClO_2^-)	(ppm as ClO_2^-)	(ppm as ClO_2^-)	(ppm as ClO_2^-)
May	0.31 ± 0.05	0.30 ± 0.03	0.33 ± 0.06	0.25 ± 0.06
June	0.30 ± 0.04	0.27 ± 0.04	0.24 ± 0.04	0.22 ± 0.02
July	0.27 ± 0.04	0.28 ± 0.01	0.30 ± 0.05	0.31 ± 0.02
August	0.30 ± 0.02	0.28 ± 0.01	*	
September	0.30 ± 0.01	0.26 ± 0.03	0.29 ± 0.04	0.28 ± 0.04
October	0.30 ± 0.04	0.33 ± 0.03	0.31 ± 0.05	0.32 ± 0.04
November	0.28 ± 0.02	0.33 ± 0.06	0.27 ± 0.04	0.25 ± 0.01
December	0.28 ± 0.02	0.29 ± 0.01	0.29 ± 0.02	0.28 ± 0.02
January	0.24 ± 0.01	0.26 ± 0.02	0.27 ± 0.02	0.27 ± 0.01
February	0.27 ± 0.02	0.30 ± 0.02	0.28 ± 0.02	0.31 ± 0.01
March	0.27 ± 0.01	0.29 ± 0.03	0.30 ± 0.03	0.30 ± 0.02
April	0.28 ± 0.04	0.30 ± 0.02	0.30 ± 0.02	0.28 ± 0.02

* No samples were collected from the fire halls in August.

Fluoride

Units; ppm (mg/L)

Month	Rossdale Reservoirs	Smith Reservoirs	Rossdale Fire halls	Smith Fire Halls
	(ppm)	(ppm)	(ppm)	(ppm)
May	1.00 ± 0.03	1.00 ± 0.02	1.02 ± 0.04	0.99 ± 0.04
June	1.01 ± 0.01	0.99 ± 0.02	1.00 ± 0.03	1.03 ± 0.02
July	0.99 ± 0.03	1.03 ± 0.03	1.00 ± 0.04	0.99 ± 0.02
August	0.99 ± 0.04	0.98 ± 0.05	*	
September	0.99 ± 0.02	1.00 ± 0.01	0.99 ± 0.03	1.00 ± 0.03
October	0.96 ± 0.02	0.98 ± 0.02	0.99 ± 0.04	1.00 ± 0.03
November	1.01 ± 0.02	0.99 ± 0.03	1.00 ± 0.02	1.01 ± 0.02
December	1.01 ± 0.01	1.00 ± 0.03	0.99 ± 0.02	0.99 ± 0.03
January	0.99 ± 0.02	1.01 ± 0.01	0.98 ± 0.03	0.99 ± 0.02
February	1.00 ± 0.02	0.99 ± 0.03	1.00 ± 0.02	0.99 ± 0.01
March	0.99 ± 0.01	0.99 ± 0.03	0.96 ± 0.03	0.99 ± 0.03
April	0.98 ± 0.03	1.00 ± 0.02	0.97 ± 0.04	0.99 ± 0.02

* No samples were collected from the fire halls in August.

Turbidity

Units; Nephelometric Turbidity Units (NTU)

Month	Rossdale Reservoirs	Smith Reservoirs	Rossdale Fire halls	Smith Fire Halls
	(NTU)	(NTU)	(NTU)	(NTU)
May	0.13 ± 0.05	0.11 ± 0.03	0.15 ± 0.10	0.12 ± 0.05
June	0.08 ± 0.03	0.06 ± 0.03	0.10 ± 0.05	0.10 ± 0.00
July	0.12 ± 0.06	0.10 ± 0.04	0.19 ± 0.13	0.17 ± 0.05
August	0.10 ± 0.01	0.09 ± 0.03	*	
September	0.14 ± 0.10	0.18 ± 0.10	0.30 ± 0.13	0.24 ± 0.12
October	0.25 ± 0.13	0.20 ± 0.06	0.26 ± 0.07	0.20 ± 0.11
November	0.28 ± 0.09	0.26 ± 0.09	0.26 ± 0.09	0.22 ± 0.05
December	0.28 ± 0.09	0.31 ± 0.08	0.38 ± 0.09	0.39 ± 0.08
January	0.30 ± 0.18	0.15 ± 0.07	0.28 ± 0.12	0.29 ± 0.13
February	0.16 ± 0.04	0.18 ± 0.06	0.10 ± 0.03	0.15 ± 0.05
March	0.12 ± 0.05	0.10 ± 0.01	0.11 ± 0.04	0.08 ± 0.03
April	0.24 ± 0.13	0.14 ± 0.03	0.15 ± 0.05	0.13 ± 0.03

* No samples were collected from the fire halls in August.

pH

Units; None

Month	Rossdale Reservoirs	Smith Reservoirs	Rossdale Fire halls	Smith Fire Halls
May	8.18 ± 0.04	8.22 ± 0.05	8.16 ± 0.05	8.20 ± 0.00
June	8.08 ± 0.08	8.25 ± 0.06	8.14 ± 0.09	8.18 ± 0.04
July	8.20 ± 0.00	8.25 ± 0.06	8.26 ± 0.10	8.32 ± 0.04
August	8.28 ± 0.04	8.27 ± 0.10	*	
September	8.24 ± 0.06	8.33 ± 0.05	8.32 ± 0.08	8.38 ± 0.08
October	8.32 ± 0.05	8.32 ± 0.05	8.35 ± 0.11	8.37 ± 0.08
November	8.27 ± 0.12	8.45 ± 0.06	8.31 ± 0.08	8.38 ± 0.08
December	8.45 ± 0.06	8.42 ± 0.05	8.39 ± 0.07	8.45 ± 0.05
January	8.35 ± 0.10	8.47 ± 0.05	8.40 ± 0.06	8.42 ± 0.04
February	8.44 ± 0.09	8.50 ± 0.01	8.37 ± 0.06	8.43 ± 0.05
March	8.36 ± 0.05	8.38 ± 0.10	8.38 ± 0.10	8.41 ± 0.15
April	8.32 ± 0.11	8.45 ± 0.06	8.25 ± 0.15	8.33 ± 0.15

* No samples were collected from the fire halls in August.

Total Hardness

Units; ppm (mg/L) as $CaCO_3$

Month	Rossdale Reservoirs	Smith Reservoirs	Rossdale Fire halls	Smith Fire Halls
	(ppm as $CaCO_3$)	(ppm as $CaCO_3$)	(ppm as $CaCO_3$)	(ppm as $CaCO_3$)
May	120 ± 5.21	114 ± 3.37	117 ± 9.04	119 ± 6.18
June	116 ± 5.47	112 ± 3.91	113 ± 2.98	112 ± 3.39
July	116 ± 3.13	112 ± 1.91	118 ± 3.02	117 ± 3.16
August	113 ± 3.27	115 ± 3.77	*	
September	113 ± 1.92	111 ± 0.96	112 ± 1.38	111 ± 1.17
October	116 ± 5.00	112 ± 4.04	116 ± 3.82	112 ± 3.44
November	113 ± 4.40	110 ± 0.50	109 ± 4.48	109 ± 3.67
December	110 ± 4.76	109 ± 2.99	109 ± 2.99	107 ± 1.17
January	112 ± 2.22	114 ± 4.27	113 ± 2.60	111 ± 2.07
February	115 ± 2.41	113 ± 2.22	116 ± 2.62	114 ± 0.98
March	114 ± 2.39	112 ± 0.50	115 ± 2.33	114 ± 2.48
April	117 ± 3.24	109 ± 1.41	111 ± 5.42	109 ± 2.56

* No samples were collected from the fire halls in August.

Calcium Hardness

Units; ppm (mg/L) as $CaCO_3$

Month	Rossdale Reservoirs	Smith Reservoirs	Rossdale Fire halls	Smith Fire Halls
	(ppm as $CaCO_3$)	(ppm as $CaCO_3$)	(ppm as $CaCO_3$)	(ppm as $CaCO_3$)
May	72 ± 2.07	68 ± 1.00	69 ± 5.71	71 ± 2.95
June	69 ± 0.84	65 ± 2.50	66 ± 2.83	66 ± 2.68
July	71 ± 2.88	68 ± 1.00	75 ± 5.11	76 ± 2.65
August	68 ± 3.67	72 ± 1.63	*	
September	69 ± 1.22	71 ± 1.70	68 ± 4.64	71 ± 2.22
October	71 ± 5.00	69 ± 1.70	70 ± 2.41	71 ± 1.22
November	69 ± 1.29	71 ± 1.29	60 ± 4.53	63 ± 1.05
December	63 ± 2.36	64 ± 1.63	59 ± 3.53	61 ± 2.56
January	61 ± 2.75	66 ± 1.73	60 ± 3.45	62 ± 1.03
February	60 ± 2.77	65 ± 1.83	64 ± 2.99	66 ± 1.37
March	64 ± 3.36	68 ± 2.06	64 ± 4.46	70 ± 1.75
April	70 ± 4.84	74 ± 1.91	76 ± 4.93	75 ± 3.01

* No samples were collected from the fire halls in August.

Total Alkalinity

Units; ppm (mg/L) as $CaCO_3$

Month	Rossdale Reservoirs	Smith Reservoirs	Rossdale Fire halls	Smith Fire Halls
	(ppm as $CaCO_3$)	(ppm as $CaCO_3$)	(ppm as $CaCO_3$)	(ppm as $CaCO_3$)
May	59 ± 5.89	49 ± 1.91	60 ± 8.74	50 ± 3.08
June	55 ± 5.45	49 ± 1.29	51 ± 5.55	47 ± 2.51
July	47 ± 2.07	46 ± 2.16	44 ± 3.56	43 ± 2.97
August	52 ± 2.07	49 ± 2.52	*	
September	58 ± 3.27	55 ± 1.26	60 ± 5.56	55 ± 3.60
October	60 ± 4.50	53 ± 0.00	64 ± 5.90	58 ± 2.66
November	64 ± 3.86	57 ± 5.62	55 ± 6.73	48 ± 1.21
December	53 ± 8.08	48 ± 3.69	52 ± 3.87	51 ± 3.72
January	58 ± 2.36	58 ± 0.97	57 ± 3.22	56 ± 2.42
February	55 ± 2.12	52 ± 2.16	57 ± 4.69	51 ± 2.92
March	56 ± 2.30	50 ± 5.29	53 ± 6.04	44 ± 1.94
April	50 ± 6.87	42 ± 0.96	47 ± 4.01	45 ± 2.48

* No samples were collected from the fire halls in August.

Soluble Organic Carbon

Units; HAU (Humic Acid Units)

Month	Rossdale Reservoirs	Smith Reservoirs	Rossdale Fire halls	Smith Fire Halls
	(HAU)	(HAU)	(HAU)	(HAU)
May	2.50 ± 0.34	2.33 ± 0.58	2.88 ± 0.43	2.42 ± 0.34
June	2.42 ± 0.49	1.56 ± 0.35	2.69 ± 0.74	2.10 ± 0.37
July	3.59 ± 0.20	2.42 ± 0.17	3.98 ± 0.70	3.17 ± 0.69
August	4.51 ± 0.21	4.13 ± 0.29	*	
September	2.96 ± 0.16	2.63 ± 0.23	2.88 ± 0.54	2.67 ± 0.30
October	2.76 ± 0.27	2.67 ± 0.38	2.32 ± 0.60	1.75 ± 0.16
November	2.60 ± 0.49	2.39 ± 0.22	2.78 ± 0.54	2.22 ± 0.19
December	1.96 ± 0.29	1.49 ± 0.50	1.90 ± 0.54	1.83 ± 0.29
January	3.60 ± 0.36	2.38 ± 0.27	3.75 ± 0.57	3.01 ± 0.40
February	3.60 ± 0.17	3.47 ± 0.08	3.61 ± 0.41	3.07 ± 0.28
March	3.98 ± 0.28	3.30 ± 0.21	3.98 ± 0.60	3.10 ± 0.04
April	4.85 ± 1.52	8.50 ± 2.59	7.36 ± 2.16	9.27 ± 2.42

* No samples were collected from the fire halls in August.

Aluminium

Units; ppb (µg/L)

Month	Rossdale Reservoirs	Smith Reservoirs	Rossdale Fire halls	Smith Fire Halls
	(ppb)	(ppb)	(ppb)	(ppb)
June	198 ± 26	195 ± 10	*	
July	244 ± 8	215 ± 24	271 ± 35	282 ± 29
August **				
September	398 ± 13	360 ± 14	351 ± 41	361 ± 50
October	335 ± 57	310 ± 56	377 ± 62	303 ± 53
November	430 ± 26	552 ± 66	382 ± 56	452 ± 85
December	313 ± 54	338 ± 89	359 ± 54	397 ± 47
January	450 ± 26	448 ± 24	444 ± 37	432 ± 29
February	306 ± 27	303 ± 26	271 ± 28	297 ± 14
March	302 ± 9	326 ± 33	279 ± 13	285 ± 14
April	278 ± 24	305 ± 48	350 ± 59	330 ± 67

* Analysis for metals was not carried out on samples collected from the fire halls in June.

** No metals analysis was carried out in August.

Cadmium

Units; ppb (µg/L)

Month	Rossdale Reservoirs	Smith Reservoirs	Rossdale Fire halls	Smith Fire Halls
	(ppb)	(ppb)	(ppb)	(ppb)
June	0.14 ± 0.06	0.15 ± 0.07	*	
July	0.12 ± 0.05	0.08 ± 0.05	0.13 ± 0.09	0.10 ± 0.00
August **				
September	0.10 ± 0.00	0.15 ± 0.06	0.13 ± 0.05	0.15 ± 0.06
October	0.15 ± 0.06	0.18 ± 0.09	0.15 ± 0.05	0.25 ± 0.16
November	0.25 ± 0.06	0.25 ± 0.06	0.23 ± 0.10	0.30 ± 0.06
December	0.10 ± 0.00	0.18 ± 0.09	0.14 ± 0.05	0.12 ± 0.04
January	0.20 ± 0.00	0.18 ± 0.05	0.17 ± 0.05	0.18 ± 0.08
February	0.10 ± 0.00	0.10 ± 0.00	0.11 ± 0.03	0.12 ± 0.04
March	0.10 ± 0.00	0.13 ± 0.05	0.12 ± 0.04	0.10 ± 0.00
April	0.20 ± 0.00	0.20 ± 0.00	0.22 ± 0.04	0.23 ± 0.05

* Analysis for metals was not carried out on samples collected from the fire halls in June.

** No metals analysis was carried out in August.

Chromium

Units; ppb (µg/L)

Month	Rossdale Reservoirs	Smith Reservoirs	Rossdale Fire halls	Smith Fire Halls
	(ppb)	(ppb)	(ppb)	(ppb)
June	0.50 ± 0.07	0.53 ± 0.05	*	
July	0.64 ± 0.09	0.55 ± 0.06	0.53 ± 0.08	0.57 ± 0.10
August **				
September	0.56 ± 0.09	0.63 ± 0.05	0.60 ± 0.10	0.57 ± 0.12
October	0.53 ± 0.05	0.73 ± 0.15	0.53 ± 0.13	0.55 ± 0.05
November	0.45 ± 0.06	0.55 ± 0.13	0.57 ± 0.09	0.58 ± 0.04
December	0.45 ± 0.17	0.48 ± 0.05	0.42 ± 0.11	0.42 ± 0.08
January	0.58 ± 0.05	0.70 ± 0.08	0.59 ± 0.09	0.67 ± 0.05
February	0.68 ± 0.13	0.60 ± 0.08	0.70 ± 0.10	0.77 ± 0.05
March	0.58 ± 0.05	0.65 ± 0.06	0.55 ± 0.08	0.65 ± 0.05
April	0.46 ± 0.11	0.45 ± 0.17	0.48 ± 0.06	0.53 ± 0.15

* Analysis for metals was not carried out on samples collected from the fire halls in June.

** No metals analysis was carried out in August.

Copper

Units; ppb (µg/L)

Month	Rossdale Reservoirs	Smith Reservoirs	Rossdale Fire halls	Smith Fire Halls
	(ppb)	(ppb)	(ppb)	(ppb)
June	1.20 ± 0.45	1.50 ± 0.58	*	
July	1.80 ± 0.45	1.25 ± 0.50	1.46 ± 0.66	1.83 ± 1.17
August **				
September	2.00 ± 0.70	1.25 ± 0.50	1.92 ± 0.95	2.67 ± 1.86
October	6.00 ± 2.28	5.25 ± 2.20	5.75 ± 3.86	5.00 ± 2.28
November	1.00 ± 0.00	1.50 ± 0.58	2.15 ± 1.46	3.17 ± 2.56
December	1.25 ± 0.50	1.00 ± 0.82	1.77 ± 0.82	2.67 ± 1.03
January	2.25 ± 1.50	1.25 ± 0.50	2.69 ± 1.65	3.67 ± 2.65
February	1.80 ± 1.79	0.75 ± 0.50	2.46 ± 1.85	2.83 ± 0.75
March	1.60 ± 0.89	0.75 ± 0.50	2.00 ± 1.00	2.33 ± 1.36
April	1.60 ± 0.54	1.25 ± 0.50	5.30 ± 3.32	10.17 ± 5.77

* Analysis for metals was not carried out on samples collected from the fire halls in June.

** No metals analysis was carried out in August.

Iron

Units; ppb (µg/L)

Month	Rossdale Reservoirs	Smith Reservoirs	Rossdale Fire halls	Smith Fire Halls
	(ppb)	(ppb)	(ppb)	(ppb)
June	11.75 ± 4.99	6.25 ± 4.78	*	
July	9.75 ± 2.87	8.50 ± 4.04	8.58 ± 5.08	9.50 ± 5.75
August **				
September	6.75 ± 3.09	8.50 ± 5.44	4.62 ± 2.47	5.33 ± 2.58
October	10.67 ± 2.88	11.50 ± 6.35	6.83 ± 2.75	7.33 ± 4.32
November	11.00 ± 6.00	5.75 ± 3.20	5.84 ± 4.28	5.66 ± 3.39
December	7.67 ± 2.52	7.00 ± 3.74	6.54 ± 4.21	5.67 ± 3.44
January	5.25 ± 3.59	2.75 ± 1.71	3.30 ± 2.53	2.33 ± 1.03
February	4.20 ± 3.34	7.25 ± 4.57	2.46 ± 1.94	2.50 ± 1.05
March	3.25 ± 2.50	2.50 ± 0.58	1.23 ± 0.44	1.50 ± 1.22
April	9.25 ± 8.14	13.00 ± 8.83	14.75 ± 3.77	15.68 ± 4.55

* Analysis for metals was not carried out on samples collected from the fire halls in June.

** No metals analysis was carried out in August.

Lead

Units; ppb (µg/L)

Month	Rossdale Reservoirs	Smith Reservoirs	Rossdale Fire halls	Smith Fire Halls
	(ppb)	(ppb)	(ppb)	(ppb)
June	1.40 ± 0.46	1.60 ± 0.46	*	
July	0.74 ± 0.06	1.03 ± 0.26	1.00 ± 0.16	1.05 ± 0.17
August **				
September	0.82 ± 0.13	0.78 ± 0.10	0.82 ± 0.08	0.78 ± 0.08
October	0.68 ± 0.13	0.75 ± 0.20	0.76 ± 0.31	0.90 ± 0.18
November	0.70 ± 0.47	0.55 ± 0.06	0.94 ± 0.35	0.83 ± 0.24
December	0.78 ± 0.05	0.85 ± 0.13	0.87 ± 0.11	0.93 ± 0.23
January	1.08 ± 0.10	0.93 ± 0.22	1.24 ± 0.10	1.18 ± 0.08
February	0.92 ± 0.05	0.88 ± 0.05	0.87 ± 0.10	0.93 ± 0.14
March	0.74 ± 0.09	0.80 ± 0.14	0.59 ± 0.31	0.72 ± 0.21
April	0.62 ± 0.11	0.63 ± 0.22	0.80 ± 0.10	0.77 ± 0.12

* Analysis for metals was not carried out on samples collected from the fire halls in June.

** No metals analysis was carried out in August.

Figure A1.1

Plot of the Cumulative Monthly Averages for Total Chloramines (as Chlorine) Against Time for the Five Rossdale Zone and the Four E.L.Smith Zone Reservoirs Over the Course of the Sampling Study. One Sample was Collected From Each Site Every Month and the The Error Bars Represent one Standard Deviation from the Average.

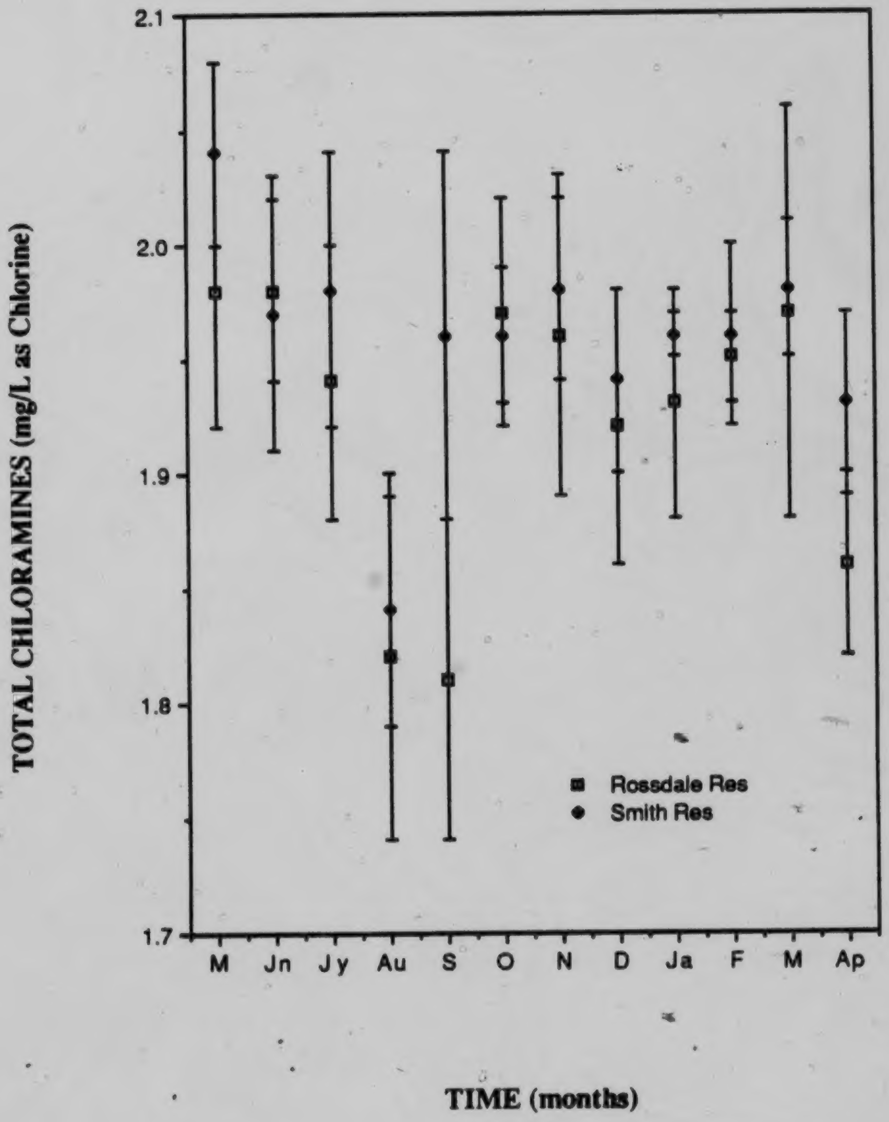


Figure A1.2

Plot of the Cumulative Monthly Averages for Total Chloramines (as Chlorine) Against Time for the Five Rossdale Zone Reservoirs and the Thirteen Rossdale Zone Fire Halls Over the Course of the Sampling Study. One Sample was Collected From Each Site Every Month and the Error Bars Represent one Standard Deviation from the Average.

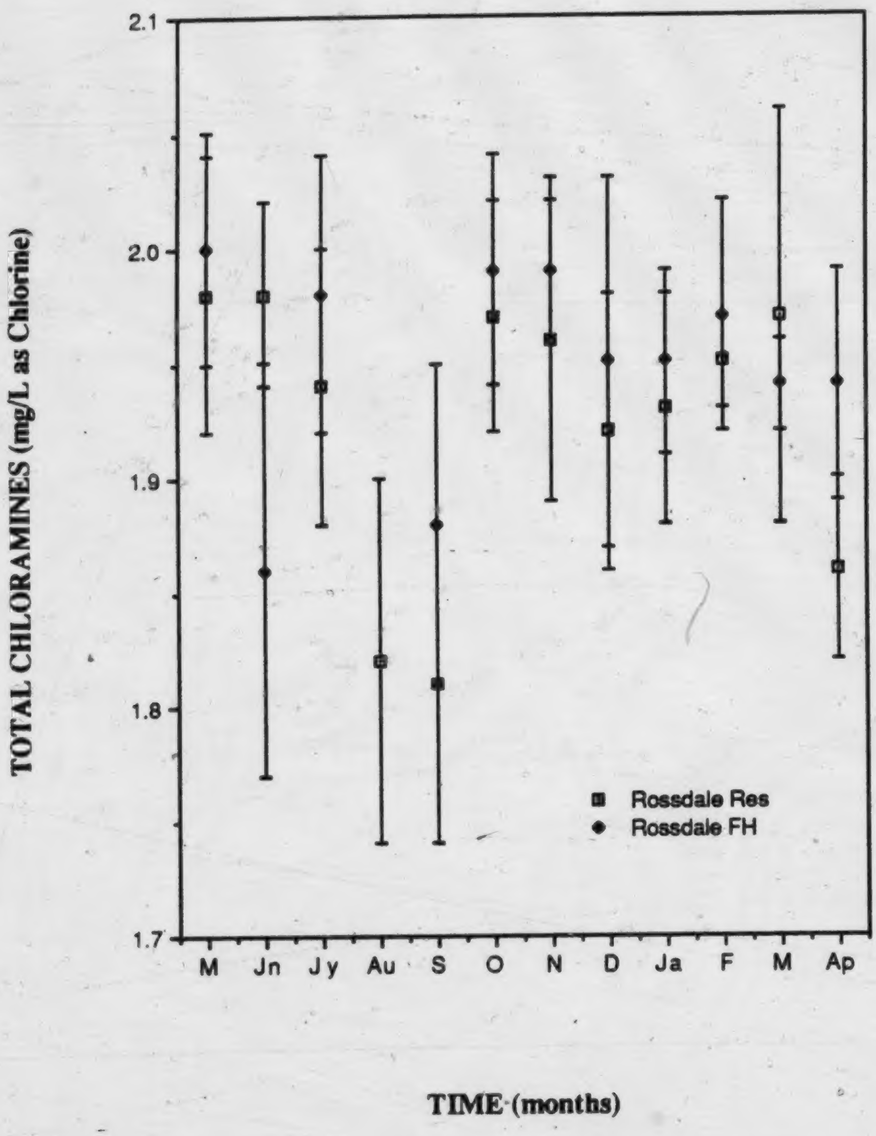


Figure A1.3

Plot of the Cumulative Monthly Averages for Total Chloramines (as Chlorine) Against Time for the Four E.L.Smith Zone Reservoirs and the Six E.L.Smith Zone Fire Halls Over the Course of the Sampling Study. One Sample was Collected From Each Site Every MonthThe Error Bars Represent one Standard Deviation from the Average.

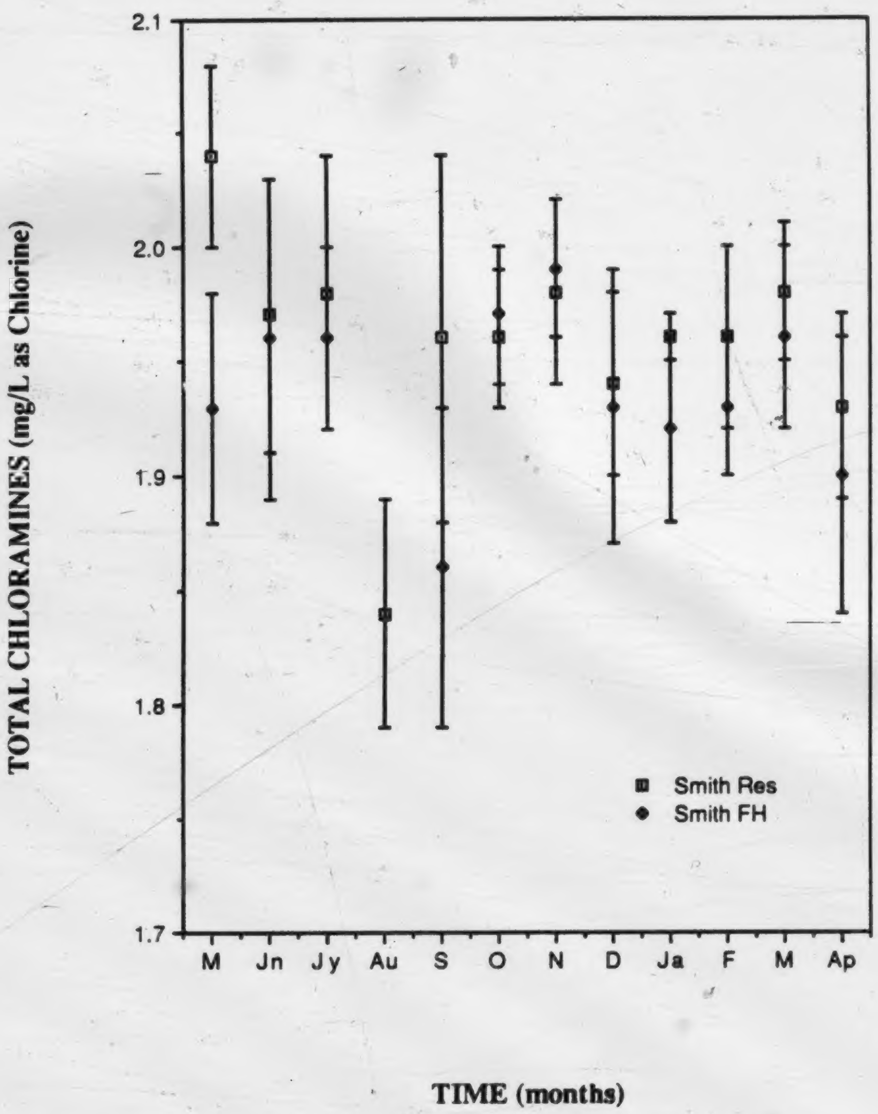


Figure A1.4

Plot of the Cumulative Monthly Averages for Total Chloramines (as Chlorine) Against Time for the Thirteen Rossdale Zone and Six E.L.Smith Zone Fire Halls Over the Course of the Sampling Study. One Sample was Collected From Each Site Every Month and the Error Bars Represent one Standard Deviation from the Average.

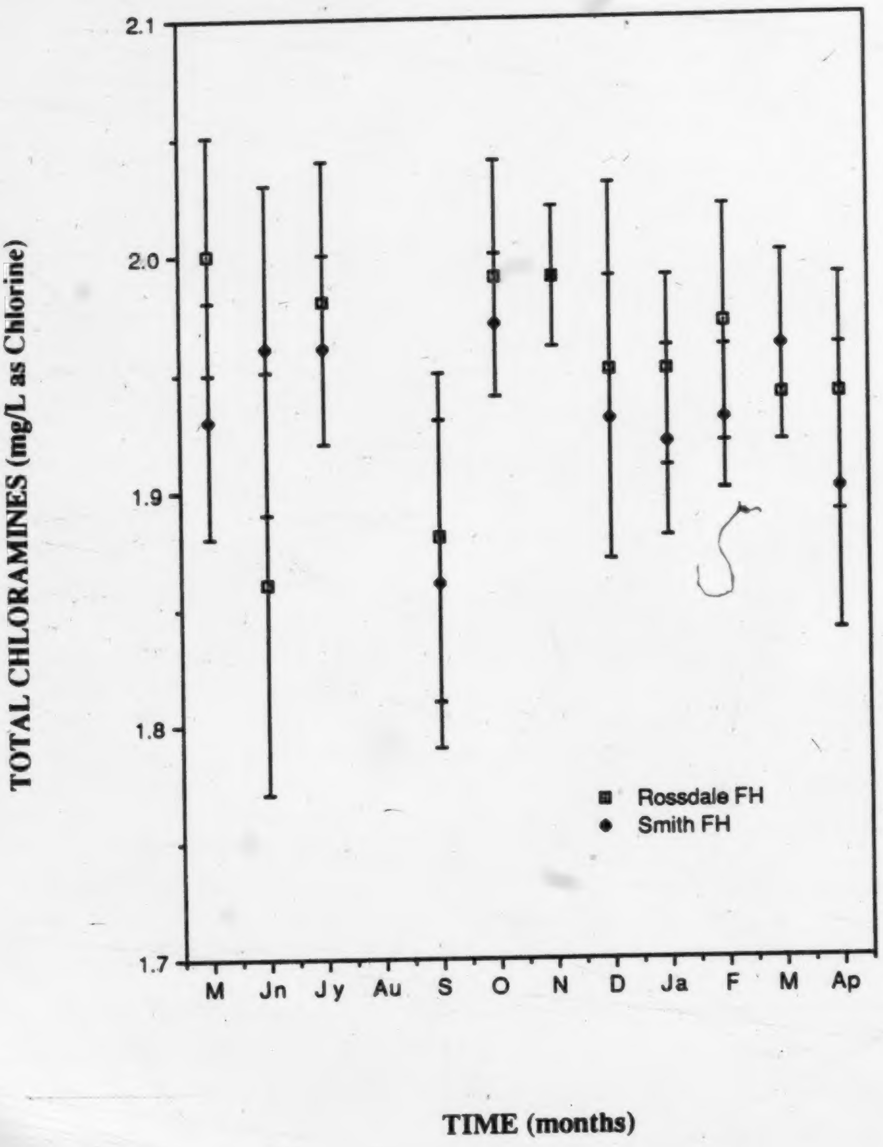


Figure A1.5

Plot of the Cumulative Monthly Averages for Turbidity Against Time for the Five Rossdale Zone and the Four E.L.Smith Zone Reservoirs Over the Course of the Sampling Study. One Sample was Collected From Each Site Every Month and the Error Bars Represent one Standard Deviation from the Average.

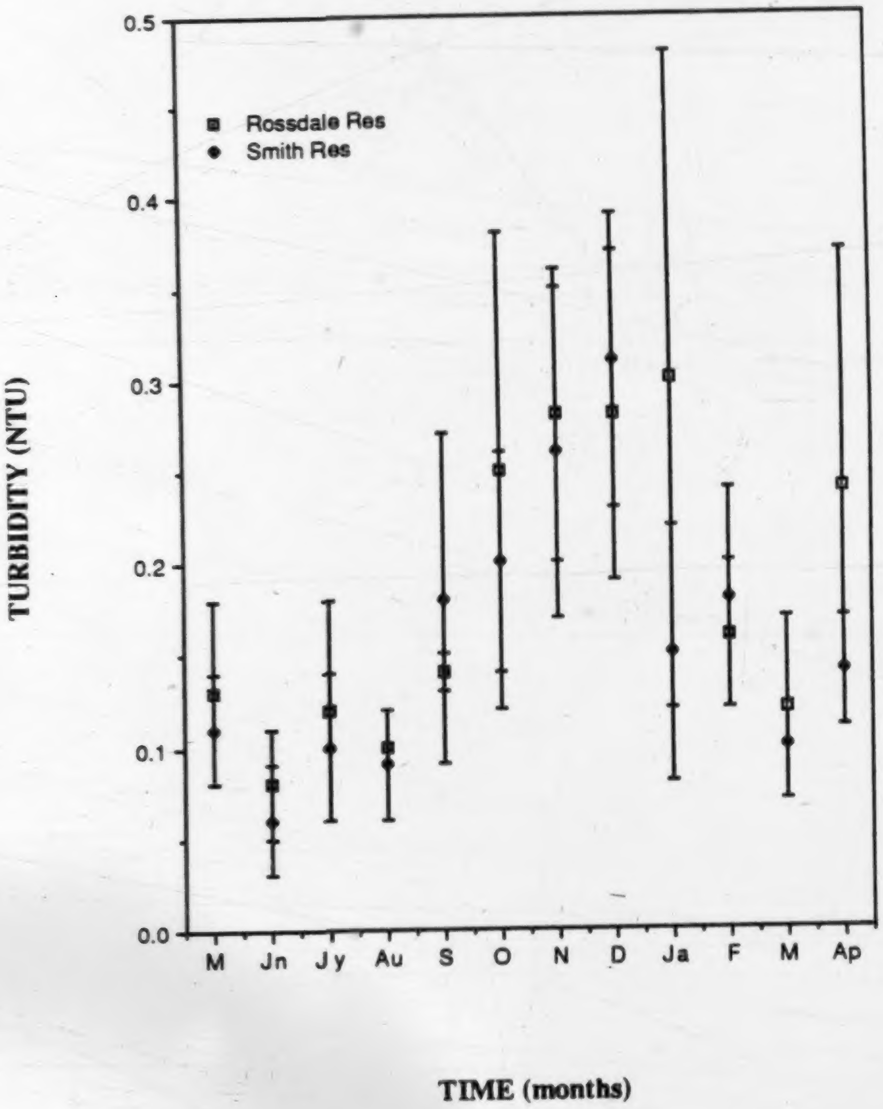


Figure A1.6

Plot of the Cumulative Monthly Averages for Soluble Organic Carbon Against Time for the Five Rossdale Zone and the Four E.L.Smith Zone Reservoirs Over the Course of the Sampling Study. One Sample was Collected From Each Site Every Month and the Error Bars Represent one Standard Deviation from the Average.

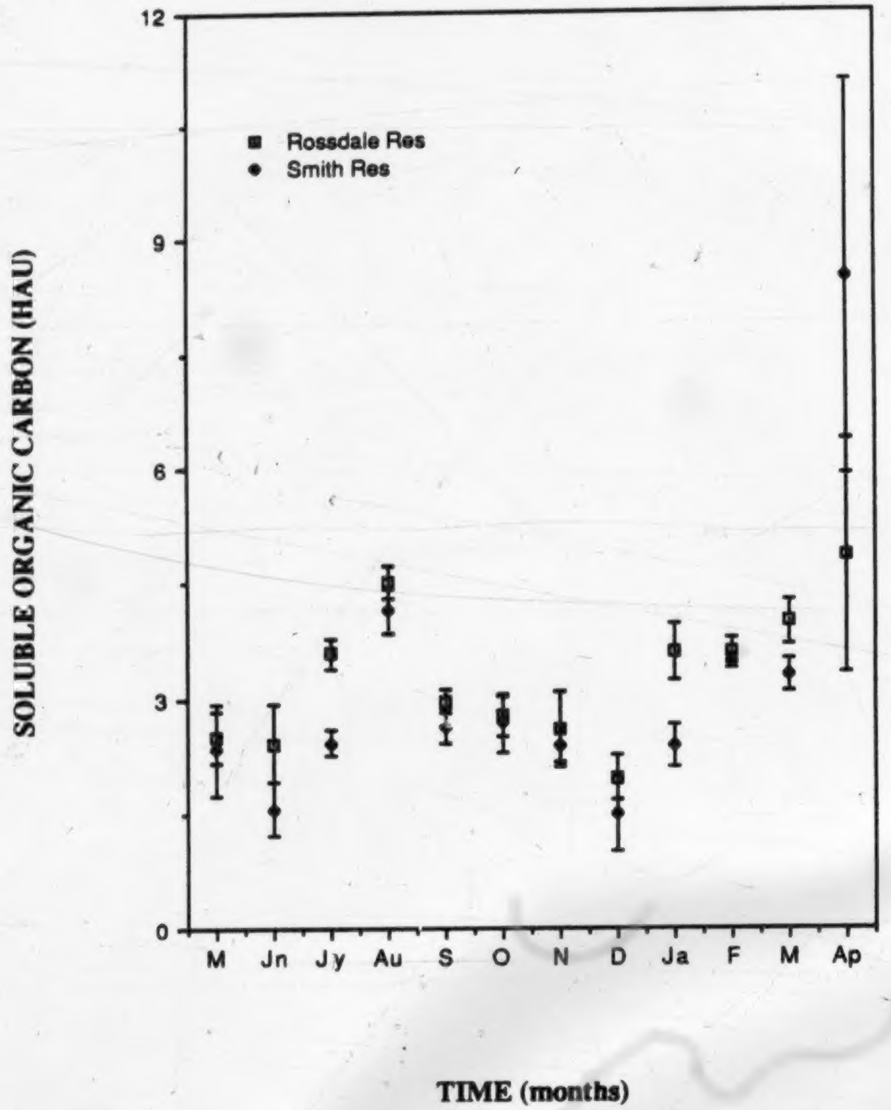


Figure A1.7

Plot of the Cumulative Monthly Averages for Soluble Organic Carbon Against Time for the Thirteen Rossdale Zone and the Six E.L.Smith Zone Fire Halls Over the Course of the Sampling Study. One Sample was Collected From Each Site Every Month and the Error Bars Represent one Standard Deviation from the Average.

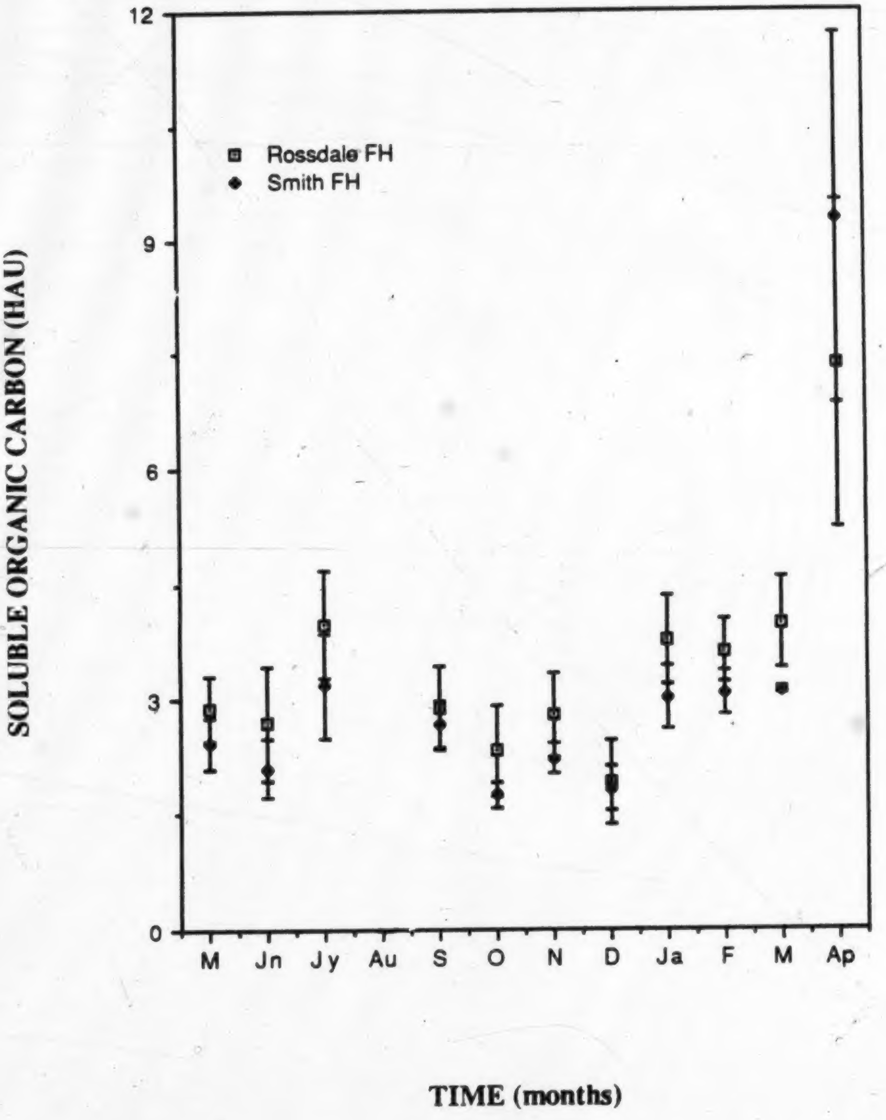


Figure A1.8

Plot of the Cumulative Monthly Averages for Aluminium Against Time for the Five Rossdale Zone and the Four E.L.Smith Zone Reservoirs Over the Course of the Sampling Study. One Sample was Collected From Each Site Every Month and the The Error Bars Represent one Standard Deviation from the Average.

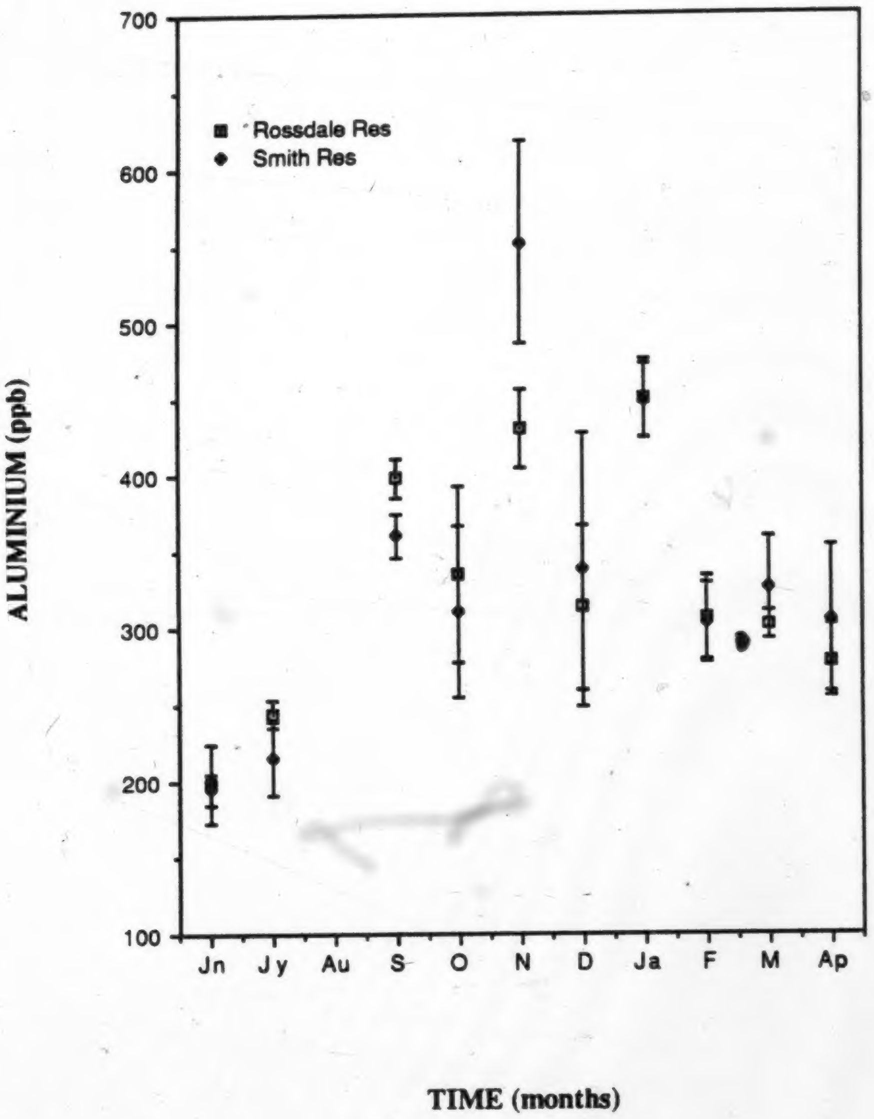


Figure A1.9

Plot of the Cumulative Monthly Averages for Copper Against Time for the Thirteen Rossdale Zone and the Six E.L.Smith Zone Fire Halls Over the Course of the Sampling Study. One Sample was Collected From Each Site Every Month and the The Error Bars Represent one Standard Deviation from the Average.

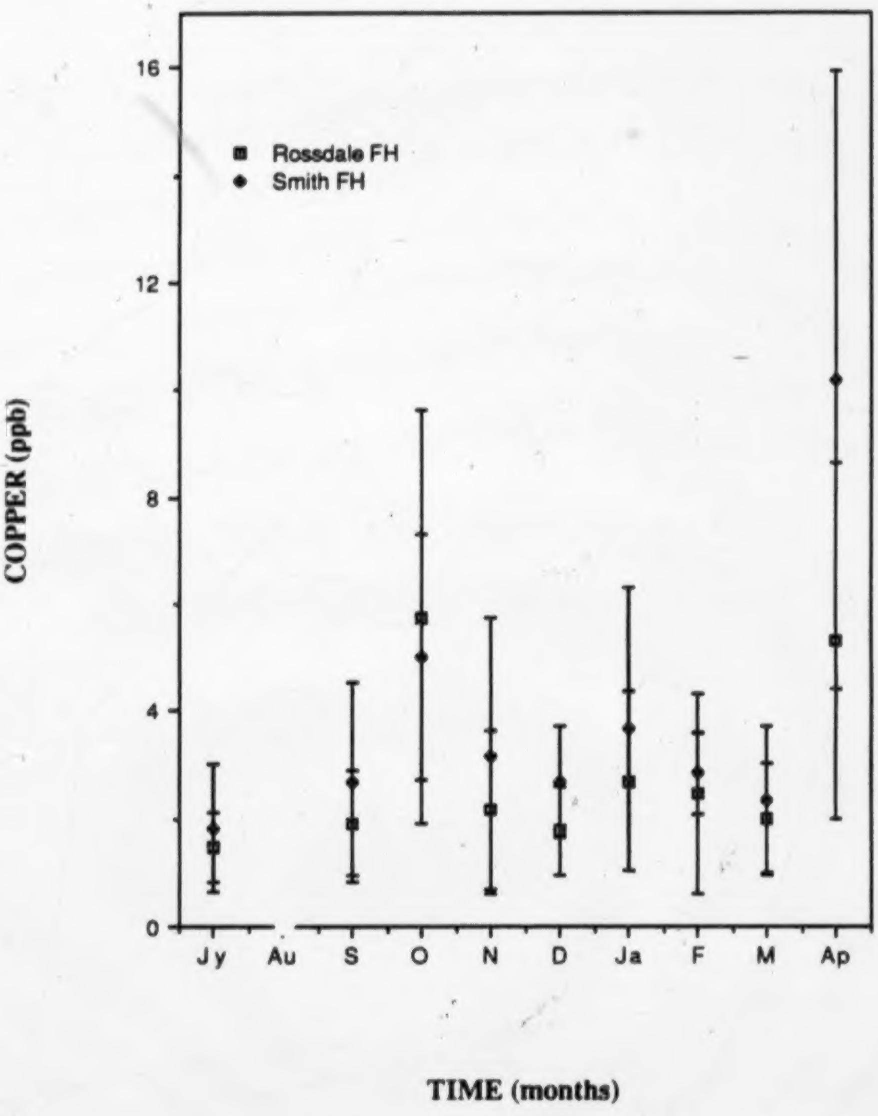
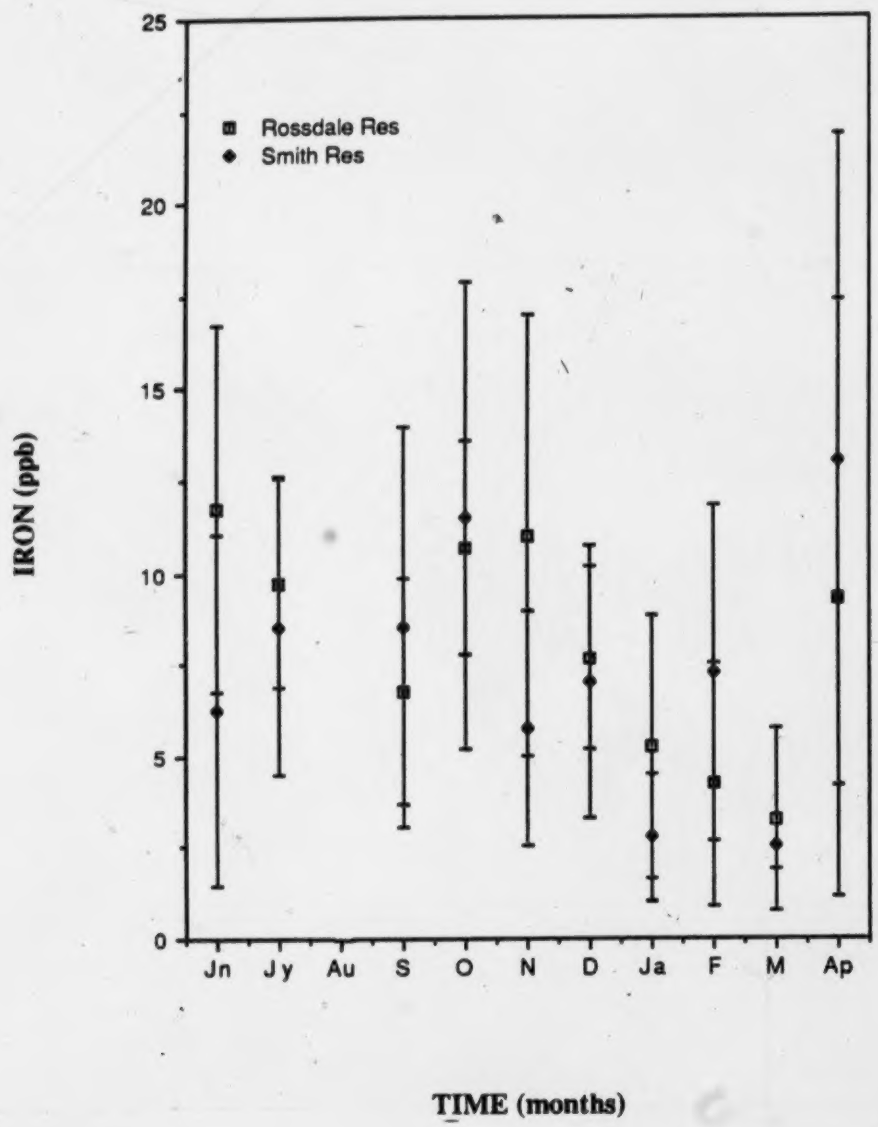


Figure A1.10

Plot of the Cumulative Monthly Averages for Iron Against Time for the Five Rossdale Zone and the Four E.L.Smith Zone Reservoirs Over the Course of the Sampling Study. One Sample was Collected From Each Site Every Month and the The Error Bars Represent one Standard Deviation from the Average.



Appendix 2

Varian SpectrAA Parameters Used for the Analysis of Metals by Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS)

This appendix contains the instrumental parameters which were used to analyze for the metals which were determined during the study on the City of Edmonton water distribution system. The parameters for aluminium, cadmium, chromium, iron and lead are shown in the following pages. The parameters used for the analysis of copper are shown on page 27 in chapter 1 of this thesis.

SpectrAA 300/400 parameters used in the analysis of Aluminium (Al) by Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS).

(a) Instrument Parameters

Instrument Mode	Absorbance
Calibration Mode	Concentration
Measurement Mode	Peak Height
Lamp current (mA)	10
Slit Width (nm)	0.5
Wavelength (nm)	309.3
Time Constant	0.05
Measurement Time (s)	1.0
Replicates	3

(b) Furnace Parameters

Step Number	Temperature (°C)	Time (sec)	Gas Flow (L/min)
1	75	5.0	3.0
2	95	50.0	3.0
3	120	10.0	3.0
4	1300	3.0	3.0
5	1300	15.0	3.0
6	1300	1.2	0.0
7	2500	1.2	0.0
8	2500	2.0	0.0
9	2700	1.0	3.0
10	2700	1.5	3.0

(c) Sampler Parameters

Solution	Conc (ppb)	Solution (μL)	Blank (μL)	Vtotal (μL)
Blank		0	10	10
Standard 1	20.0	2	8	10
Standard 2	40.0	4	6	10
Standard 3	60.0	6	4	10
Standard 4	80.0	8	2	10
Standard 5	100.0	10	0	10
Sample		10	0	10

Recalibration (Reslope) rate = every 10 samples

SpectrAA 300/400 parameters used in the analysis of Cadmium (Cd) by Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS).

(a) Instrument Parameters

Instrument Mode	Absorbance
Calibration Mode	Concentration
Measurement Mode	Peak Height
Lamp current (mA)	4
Slit Width (nm)	0.5
Wavelength (nm)	228.8
Time Constant	0.05
Measurement Time (s)	1.0
Replicates	3

(b) Furnace Parameters

Step Number	Temperature (°C)	Time (sec)	Gas Flow (L/min)
1	85	5.0	3.0
2	90	50.0	3.0
3	120	10.0	3.0
4	275	2.0	3.0
5	275	15.0	3.0
6	275	1.2	0.0
7	1800	1.3	0.0
8	1800	2.0	0.0
9	2000	1.0	3.0
10	2000	1.5	3.0

(c) Sampler Parameters

Solution	Conc (ppb)	Solution (µL)	Blank (µL)	Vtotal (µL)
Blank		0	25	25
Standard 1	0.4	1	24	25
Standard 2	0.8	2	23	25
Standard 3	1.2	2	22	25
Standard 4	2.0	5	20	25
Standard 5	4.0	10	15	25
Sample		25	0	25

Recalibration (Reslope) rate = every 10 samples

SpectrAA 300/400 parameters used in the analysis of Chromium (Cr) by Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS).

(a) Instrument Parameters

Instrument Mode	Absorbance
Calibration Mode	Concentration
Measurement Mode	Peak Height
Lamp current (mA)	7
Slit Width (nm)	0.2
Wavelength (nm)	357.9
Time Constant	0.05
Measurement Time (s)	1.0
Replicates	3

(b) Furnace Parameters

Step Number	Temperature (°C)	Time (sec)	Gas Flow (L/min)
1	80	15.0	3.0
2	95	50.0	3.0
3	130	10.0	3.0
4	1000	2.0	3.0
5	1000	15.0	3.0
6	1000	1.2	0.0
7	2500	1.2	0.0
8	2500	2.0	0.0
9	2700	0.5	3.0
10	2700	1.0	3.0

(c) Sampler Parameters

Solution	Conc (ppb)	Solution (μL)	Blank (μL)	Vtotal (μL)
Blank		0	40	40
Standard 1	0.2	2	38	40
Standard 2	0.5	4	36	40
Standard 3	1.0	8	32	40
Standard 4	3.0	24	16	40
Standard 5	5.0	40	0	40
Sample		40	0	40

Recalibration (Reslope) rate = every 10 samples

SpectrAA 300/400 parameters used in the analysis of Iron (Fe) by Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS).

(a) Instrument Parameters

Instrument Mode	Absorbance
Calibration Mode	Concentration
Measurement Mode	Peak Height
Lamp current (mA)	5
Slit Width (nm)	0.2
Wavelength (nm)	248.3
Time Constant	0.05
Measurement Time (s)	1.0
Replicates	3

(b) Furnace Parameters

Step Number	Temperature (°C)	Time (sec)	Gas Flow (L/min)
1	85	5.0	3.0
2	90	50.0	3.0
3	120	10.0	3.0
4	750	2.0	3.0
5	750	15.0	3.0
6	750	1.2	0.0
7	2300	0.9	0.0
8	2300	2.0	0.0
9	2300	1.0	3.0
10	2500	1.5	3.0

(c) Sampler Parameters

Solution	Conc (ppb)	Solution (μL)	Blank (μL)	Vtotal (μL)
Blank		0	20	20
Standard 1	2.0	2	18	20
Standard 2	5.0	5	15	20
Standard 3	10.0	10	10	20
Standard 4	15.0	15	5	20
Standard 5	20.0	20	0	20
Sample		20	0	20

Recalibration (Reslope) rate = every 8 samples

SpectrAA 300/400 parameters used in the analysis of Lead (Pb) by Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS).

(a) Instrument Parameters

Instrument Mode	Absorbance
Calibration Mode	Concentration
Measurement Mode	Peak Height
Lamp current (mA)	5
Slit Width (nm)	0.5
Wavelength (nm)	283.3
Time Constant	0.05
Measurement Time (s)	1.0
Replicates	3

(b) Furnace Parameters

Step Number	Temperature (°C)	Time (sec)	Gas Flow (L/min)
1	80	15.0	3.0
2	95	50.0	3.0
3	120	10.0	3.0
4	375	2.0	3.0
5	375	15.0	3.0
6	375	1.2	0.0
7	2000	1.2	0.0
8	2000	2.0	0.0
9	2300	1.0	3.0
10	2300	1.5	3.0

(c) Sampler Parameters

Solution	Conc (ppb)	Solution (μL)	Blank (μL)	Vtotal (μL)
Blank		0	40	40
Standard 1	0.5	2	38	40
Standard 2	1.0	4	36	40
Standard 3	3.0	12	28	40
Standard 4	5.0	10	30	40
Standard 5	10.0	40	0	40
Sample		40	0	40

Recalibration (Reslope) rate = every 10 samples